SPSE

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SCIENCE AND ENGINEERING

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Photographic Science and Engineering is dedicated to the advancement of the knowledge and application of photography and other directly related sciences. Its pages are open to all who wish to report on new studies dealing with the theory of photosensitive systems, the design of photographic instruments and apparatus useful in the treatment of photographic materials, photographic optics and illuminants, the use of photography for scientific or engineering measurement or recording, and photographic instrumentation and data recording. Only original papers should be submitted except on special invitation.

Manuscripts should be typed double-spaced on white bond paper with $1\frac{1}{4}$-in. margins all around. Literature references should be exact, and should include titles of journals, names of authors, numbers of volumes and pages, and year of publication. Book references should include title of volume, names of authors, publisher, number of edition, year of publication, and chapter and pages cited.

Graphs, charts, and other line illustrations should conform to good usage such as given in the American Standards Association Document Y-15, "A Guide for Preparing Technical Illustrations for Publication and Projection." Continuous-tone photographs should be made on 8- by 10-inch glossy paper and should show pertinent image detail sufficiently clearly to permit reduction to fit a 3-in. column in this journal. All illustrations should be numbered in soft blue pencil on the back to correspond with captions typed on a separate page. Tables should also be submitted on separate pages appropriately identified. An abstract should accompany each manuscript.

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New Honorary Member

Douglas A. Spencer

Dr. Douglas A. Spencer, photographic scientist, teacher, and administrator, revealed an interest in the study and use of photography when he was at the University of London in the early twenties. It was a good environment. Abney had had his lab there in South Kensington, while in a sister college Ramsay had been professor and Mees and Sheppard had done their classical researches under his guidance. It is clear that the aura influenced Dr. Spencer many years later.

With characteristic precocity, just after graduation he entered a firm of photographic consultants—a function usually sought by men approaching retirement. He was in fact from 1926 to 1939, a Director of Murray, Bull, and Spencer, Consulting Chemists. It was in this period that he was involved in the exploitation of the diazo-type processes in their early days. He also became interested in color photography and formed one of the better firms for providing color photographs for professionals, Colour Photographs Ltd., using an improvement of the carbro process—Vivex. This led to the realization that something had to be done about improving the printing of color photographs, and so from 1937 to 1939 we find him Managing Director of Linked Engraving Company—the "Linked" in this case referring to the relationship between the photograph and the printing.

Dr. Spencer joined Kodak Limited in England about the outbreak of war in 1939, as a member of the Research Laboratory in Charge of Government Projects. From 1942 to 1945, he was Principal Scientific Officer at the British Ministry of Aircraft Production in Charge of Research and Development of Air Photography for the RAF. During this time, he was also Secretary of the Air Photography Research Committee, Ministry of Aircraft Production.

After the war, he returned to Kodak as technical advisor to the management and rapidly advanced to his present position as Managing Director of the Kodak Company in England. His untiring energy, his gift of the language, his full experience in his field, and his infectious wit have endeared him to audiences in Europe and this country.

Many technical organizations in Great Britain have accorded him honors. He is a Fellow of the Royal Photographic Society, the Institute of British Photographers, and the Royal Institute of Chemistry. From 1935 to 1937, he served as President of the Royal Photographic Society.

For almost forty years, he has been a strong influence in the applied aspects of photography over an unusually wide range of subjects. In most of these, he became a leading authority. A glance at his published papers reveals the versatility of his interests. Starting in his college days and in conjunction with K. C. D. Hickman, he published a series of six classical papers on washing photographs. Later papers concerned diazo and other engineering-drawing reproduction processes; a range of papers on color photography (including one entitled "Humbug in Color Photography"); studies of accuracy in color reproduction, particularly by the photogravure process; studies of the Dufaycolor additive process; and Vivex, a modification of the carbro process. Also included were a variety of papers on special subjects, such as testing safety glass, dazzle-free flash photography, causes of graininess, the effect of silver ion reactants on developers, and many papers and a book on special applications of photography—including aerial, engineering, industrial, geographical, forestry, and ecology. His book *Color Photography in Practice* is still a classic. His knowledge, judgment, and energy have been applied recently to editing the three volumes of *Progress in Photography*. In addition, he has a book on motion-picture photography, and, with W. Randerson, he even wrote a science-fiction book, *The North Sea Monster*.

Douglas Spencer is a very human person, his hobbies including painting, gardening, and his young children. In a recent letter he wrote, "I am still a bit staggered at finding myself creeping into a bracket with some really great men. I feel there are only three contributions to science of which I am proud because, though minor enough, they were my own—the first, nothing to do with photography, was preparing and isolating triazobromide in my twenties and wrecking a good deal of my lab in the process; second, the discovery that, despite A. J. Bull and C. E. K. Mees on the subject, square-cut (referring to transmittance) filters are *not* the ideal for color reproduction; and third, the real underlying reasons why copying a (color) photograph is typically an unsatisfactory thing to do, and a most important practical, though laborious, way of overcoming it when important to do so."

Dr. Spencer has made great contributions to the branches of photography in which this Society has a special interest. The Society of Photographic Scientists and Engineers is proud to add to his many honors the highest that it can bestow, Honorary Membership in the Society, ". . . in recognition of his lifelong eminent service and outstanding leadership in the advancement of photographic science."—*Walter Clark*

PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 4, Number 4, July-August 1960

Thiourea and Its Derivatives in Photographic Stabilization Processing

ROLF S. BRUENNER,* *U.S. Army Signal Research and Development Laboratories, Fort Monmouth, N.J.*

Restrictions are placed on stabilizing processing by formation of fog if the alkaline developer is contaminated with thiourea, by fading of stabilized prints on regular paper base at high humidity, and by stickiness of the gelatin layer caused by thiourea processing at elevated temperatures. Tests were made of all methyl and some other derivatives of thiourea to determine their stabilizing characteristics and their possible use as substitutes for thiourea. To improve the stabilization characteristics of thiourea, the silver thiourea complex was protected from decomposition by increasing the bromide concentration in a paper developer without undue decrease in gamma or developing time. The silver image was protected by additives (selenium or gold toning) and excessive swelling of the gelatin was reduced by use of highly concentrated thiourea solutions at elevated temperatures. A probable fading mechanism and the use of a possible intermediate as a bleach bath component are discussed.

The term *stabilization*, unfortunately, has two meanings in photography. When applied to the manufacture of emulsions, it means the techniques used to prepare the emulsions in such a manner that they will not change their characteristics with time and under adverse storing conditions; in particular, that they will not develop excessive fog. When applied to the processing of exposed film and paper, *stabilization* means the conversion of undeveloped silver halide into a complex compound that is not light sensitive, is transparent, and can be left in the gelatin without ill effects on the image quality and/or the gelatin.

Stabilization processing has been introduced as a means for eliminating washing. In military operations, water for washing may not be available, and the time saved by eliminating one step in the process is frequently important. Current stabilizing processes use thiosulfate, thiocyanate (Grant Process), or thiourea.[1] All but the last need a rinse.

Stabilization with Thiourea

Potential sources of trouble in stabilization by thiourea are:

(1) The silver thiourea complex is not stable at pH>7, but decomposes into silver sulfide and cyanamide.

(2) Metallic silver is converted into the silver thiourea complex by excess thiourea and aerial oxygen ("fading" of the silver image).

(3) The thiourea tends to make the wet gelatin layer sticky, especially at elevated temperatures or higher concentrations.

The developer and stabilizing solutions now used with this process are designed to prevent the sources of trouble mentioned above. The formulations used[1] are shown in Table I.

The developer is used at pH 7, which prevents the formation of fog if contamination with stabilizing solution occurs. The stabilizing solutions are dilute compared to a saturated solution of thiourea which, at room temperature, contains about 100 grams/liter. A special type of paper with a water-resistant base is used, and the stop bath serves at the same time as a hardening bath.

Stabilization by Thiourea after Development by Regular Metol-Hydroquinone Developers

It is also desirable to use stabilization processing with alkaline Metol-hydroquinone developers and with regular printing paper. Such developers have not been used previously because of the possible formation of fog if contamination with thiourea solution occurs. A comparison was made, therefore, of the effect of contamination of developers (Kodak D-19 and D-72 and amidol) with stabilizing solution on fog, gamma, and speed of film and printing paper.

Film (Kodak Super Tri-X): The developer was contaminated by increasing amounts of stabilizing solution (up to 10 ml/liter of developer). Figures 1-3 show that fog remains constant with up to 5 ml stabilizer solution per liter of Kodak D-19 Developer.

Presented at the National Conference, Chicago, 30 October 1959. Received 15 September 1959; revised 15 April 1960.

* Present address: Aerojet-General Corp., Sacramento, Calif.

1. H. D. Russell, U.S. Patent 2,453,346, Nov. 9, 1948.
———, E. C. Yackel, and J. S. Bruce, *PSA Jour. (Phot. Sci. & Tech.)*, **16B**: 59 (1950).
S. Levinos and W. C. Burner, *Phot. Eng.*, **2**: 145 (1951).
——— and ———, U.S. Patent 2,696,439, Dec. 7, 1954.

TABLE I — Processing Formulas for Stabilization with Thiourea

Temperature—68°F; Developer pH—7

		For film		For paper (waterproof)	
Developer	Amidol	7.2 grams/liter	3 min	7.2 grams/liter	1 min
	$(NH_4)_2SO_3$	63 grams/liter		63 grams/liter	
	KBr	2.1 grams/liter		4.2 grams/liter	
Stop bath	Chrome alum	31.5 grams/liter	1.5 min	———	
	$NaHSO_3$	———		31.5 grams/liter	2 min
Stabilizer	Thiourea	31.5 grams/liter	3 min	15.8 grams/liter	2 min
	Glycerine	10.5 ml/liter		5.3 ml/liter	

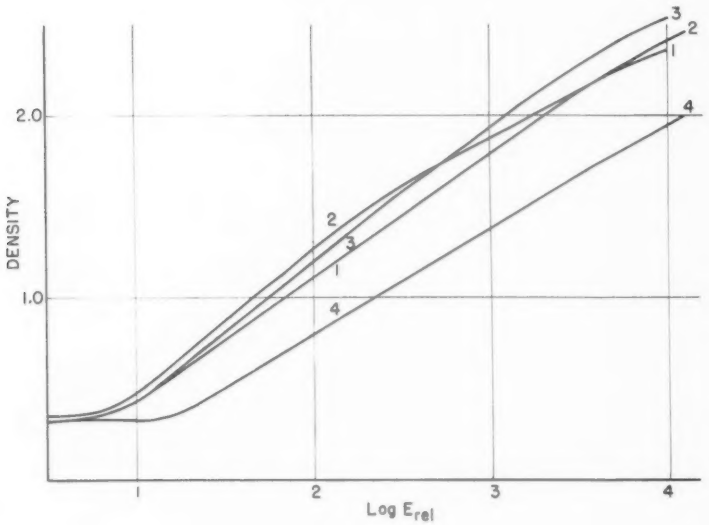


Fig. 1. Effect of different processing procedures on gamma and speed of Kodak Super Tri-X Film.

Curve 1. Processing sequence: Kodak D-19 Developer (5 min); Kodak SB-1a Stop Bath; Kodak F-5 Fixer (hypo); wash.

Curve 2. D-19; SB-1a; ethylenethiourea stabilizing solution.

Curve 3. D-19; SB-1a; thiourea stabilizing solution.

Curve 4. Amidol developer; chrome alum stop; thiourea stabilizing solution.

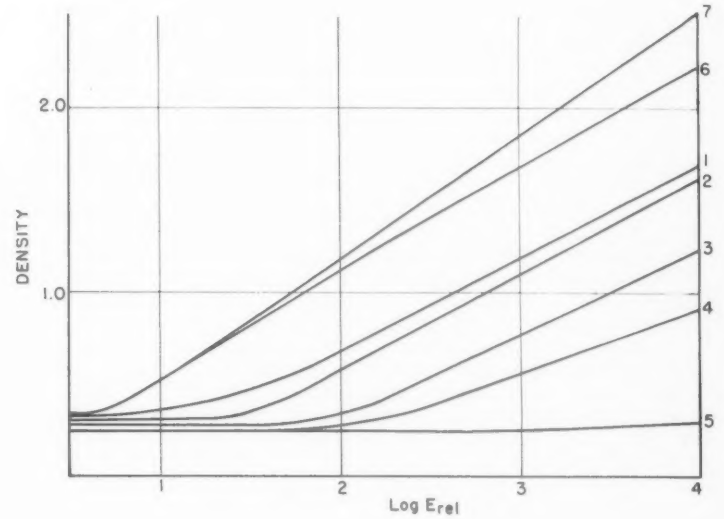


Fig. 2. Effect of contaminating the developer by adding thiourea stabilizing solution to it. Kodak Super Tri-X Film.

Curve 1. Processing sequence: Amidol developer (2¾ min); chrome alum stop; thiourea stabilizing solution.

Curve 2. As 1, but with 0.5 ml stabilizing solution added per liter of developer.

Curve 3. As 1, but 1.5 ml stabilizing solution/-liter.

Curve 4. As 1, but 4.5 ml stabilizing solution/-liter.

Curve 5. As 1, but 10.0 ml stabilizing solution/-liter.

Curve 6. As 1, except 5 min development.

Curve 7. Processing sequence: D-19 (5 min); SB-1a; thiourea stabilizing solution.

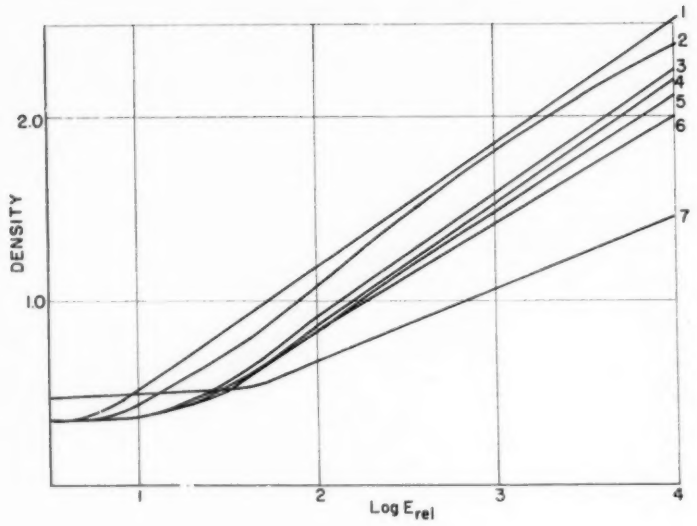


Fig. 3. Effect of contaminating Kodak D-19 Developer by adding thiourea stabilizing solution to it. Kodak Super Tri-X Film.

Curve 1. Processing sequence: D-19 (5 min); SB-1a; thiourea stabilizing solution.

Curve 2. As 1, but with 0.5 ml stabilizing solution added per liter of developer.

Curve 3. As 1, but 1.0 ml stabilizing solution/-liter.

Curve 4. As 1, but 2.0 ml stabilizing solution/-liter.

Curve 5. As 1, but 3.5 ml stabilizing solution/-liter.

Curve 6. As 1, but 5.0 ml stabilizing solution/-liter.

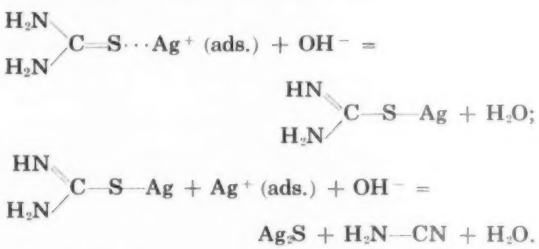
Curve 7. As 1, but 10.0 ml stabilizing solution/-liter.

Fog increases only after 10 ml/liter ($D_{fog}=0.15$), whereas with amidol developer it decreases gradually. With 10 ml/liter of amidol developer, the decrease is about $D=0.1$. Gamma and speed, however, decrease more with the amidol developer when the stabilizing solution is added than with D-19.

Printing paper (*Varigam and Halobrome, Grade 3*): Contamination of the developer (D-72 and amidol) with stabilizing solution produces different fog-formation results with paper than with film. On adding stabilizing solution to an alkaline developer, excessive fog is formed on paper; moreover, the characteristic curve shows a minimum, which means a reversal in the first portion of the curve (Fig. 4). With neutral amidol developer this phenomenon will not be seen, but, as with film, the gamma for the paper will decrease considerably.

The excessive fog formation and the partial reversal can be completely avoided if the potassium bromide concentration of the alkaline developer is decreased, e.g., from 0.6 (D-72) to 5 grams/liter. This will not decrease the rate of development substantially; the gamma will be only slightly lower or, with Halobrome (Fig. 6), essentially the same. Other antifoggants, e.g., benzotriazole, are of no special use.

These results can be understood on the basis of studies made by T. H. James and W. Vanselow[2,3] and others[4] on the decomposition of thiourea, adsorbed to silver bromide, into silver sulfide. The rate of Ag_2S formation was found to be proportional to between the first and second power of the hydroxyl ion concentration and to the logarithm of the silver ion concentration (surface reaction). The following equations represent the chemical reaction:



Probably these equations are applicable to the formation of silver sulfide in solution from $[Ag(thiourea)]^+$ and a dependence on the hydroxyl and silver ion concentrations can also be expected. This explains the excessive fog formation with photographic paper, which usually contains a certain amount of AgCl. The silver ion concentration is increased; it can be reduced by addition of bromide ions, and fog will be suppressed.

To prevent stain from carry-over of developer to the stabilizing solution, the silver ion concentration can be decreased by increasing the thiourea concentration. Inth is way, not only the silver ion concentration but also the concentration of the $[Ag(thiourea)]^+$ ion, which is the starting compound for the Ag_2S formation, is decreased:

$$Ag^+ + \text{thiourea} = [Ag(\text{thiourea})]^+;$$

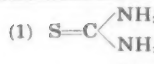
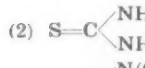
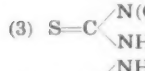
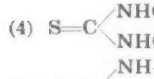
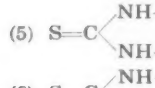
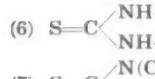
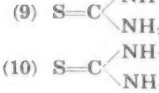
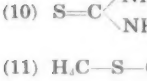
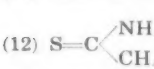
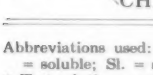
$$[Ag(\text{thiourea})]^+ + (n-1)\ \text{thiourea} = [Ag(\text{thiourea})_n]^+ \text{ (see Ref. 5).}$$

Characteristics of Thiourea Derivatives

Since the decomposition of the silver thiourea complex depends on the elimination of a proton, electron donor groups such as methyl should increase the

2. T. H. James and W. Vanselow, *J. Phys. Chem.*, **57**: 725 (1953).
3. ——— and ———, *J. Phot. Sci.*, **1**: 133 (1953).
4. R. B. Collins and H. O. Dickinson, *Sci. Ind. Phot.* (2), **23**: 92 (1952).

TABLE II — Characteristics of Thiourea and Its Derivatives

Structural formula	Reaction with $AgNO_3$ at pH>7*	Fixing characteristics†	Solubility of silver compound‡
(1) 	Fast decompn.	Short fix. time	Sl. sol.
(2) 	Slower than 1, but still fast	Short fix. time	Very sol.
(3) 	Moderate decompn.	Crystallization, opaque	Very sol.
(4) 	Moderate to slow decompn.	Crystallization, turbid	Sl. sol.
(5) 	No decompn.	Long fix. time	Very sl. sol.
(6) 	No decompn.	Turbid	Sl. sol.
(7)	Very slow decompn.	Long fix. time	Very sol.
(8)	No decompn.	Crystallization, opaque	Very sol.
(9) 	Fast decompn.	Opaque	Sl. sol.
(10) 	Fast decompn.	Opaque	Sl. sol.
(11) 	Fast decompn. (Ag-mercaptide)	——	——
(12) 	Fast decompn.	——	——

Abbreviations used: Decompn. = decomposition; Fix. = fixing; Sol. = soluble; Sl. = slightly.

* Test solutions contained the corresponding derivative, $AgNO_3$, and an alkaline agent; molar ratios, 5:1:1. Alkaline agents: NH_3, Na_2CO_3, and NaOH; tests run at room and elevated temperatures.

† 0.2 mol. solutions at room temperature with film.

‡ Solutions containing the derivative and $AgNO_3$; molar ration, 1:1 The solubility differences are very marked; either there is a bulky precipitate or no precipitate at all.

inherent stability of these silver complexes against alkaline decomposition. The results with some thiourea derivatives are listed in Table II; they are in agreement with other publications.[2,3,6] It can be seen from the table that the stability of the corresponding silver complexes increases with the increasing number of methyl groups attached to the nitrogen. As can be expected, the asymmetric N,N-dimethylthiourea is less stable than its symmetric N,N′ isomer, but is more stable than monomethylthiourea.

Remarkable exceptions in this series are those derivatives which form a heterocyclic ring (Compounds 5 and 6, Table II). Although the stability of their silver complexes is higher than that with thiourea, the corresponding silver ion concentrations differ only by a factor of ten (the silver ion concentration of a mixture of 2 parts 0.1 *M* thiourea with 1 part 0.1 *M* $AgNO_3$ is about ten times higher than that of a corresponding mixture of ethylenethiourea and silver nitrate), and cannot explain their outstanding resistance to alkaline decomposition. An amidinium-type resonance might be favored by the ring closure, which allows no rotation of the amide groups.

The absorption spectra of Compounds 1–7 are very similar, whereas the spectrum of tetramethylthiourea (Compound 8) is definitely different.[7] Peak absorption of all but the last is much closer to the wavelength of an amidinium salt than to that of thioacetamide. (All absorptions were measured in 5×10^{-5} molar aqueous solutions. Slight differences of the pH of these solutions, due to the nature of each derivative, do not affect the absorption. The absorption of thiourea is practically the same in a nearly neutral aqueous solution, in 0.01 *M* NaOH, and in 0.1 *M* NaOH. The shape of the curve and the absorption maximum remain unchanged, while

5. K. B. Yatsimirskii and A. A. Astasheva, *Zhur. Fiz. Khim.*, **27:** 1539 (1953).

6. S. Suzuki and T. Kataoka, *Phot. Sci. & Eng.*, **3:** 127 (1959).

7 H. Rivier and J. Borel, *Helv. Chim. Acta*, **11:** 1219 (1928).

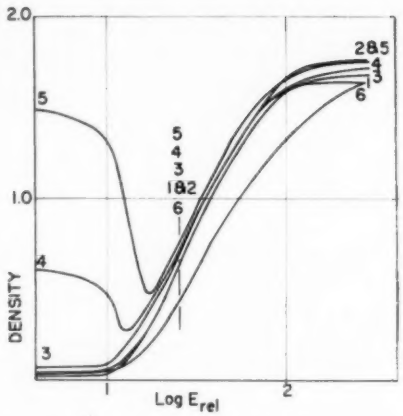


Fig. 4. Effect of contaminating Kodak D-72 Developer by adding thiourea stabilizing solution to it. Varigam paper (water-resistant base); infrared drying.

Curve 1. Processing sequence: D-72 (2 min); SB-1; hypo; wash.
Curve 2. Processing sequence: D-72 (2 min); SB-1; thiourea stabilizing solution.
Curve 3. As 2, but with 0.5 ml stabilizing solution added per liter of developer.
Curve 4. As 2, but 1.5 ml stabilizing solution/liter.
Curve 5. As 2, but 4.5 ml stabilizing solution/liter.
Curve 6. As 5, but with 4.4 grams KBr added per liter of developer.

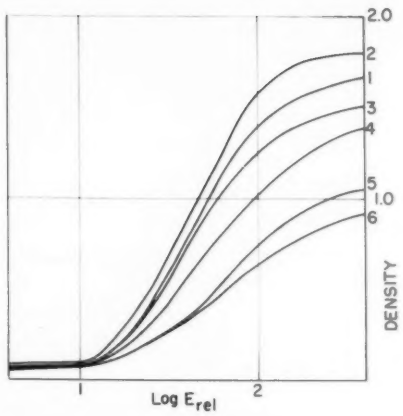


Fig. 5. Effect of contaminating amidol developer by adding thiourea stabilizing solution to it. Varigam paper (water-resistant base); infrared drying.

Curve 1. Processing sequence: amidol (1 min); $NaHSO_3$ stop solution; thiourea stabilizing solution.
Curve 2. As 1, but 2 min development.
Curve 3. As 1, but with 0.5 ml stabilizing solution added per liter of developer.
Curve 4. As 1, but 1.5 ml stabilizing solution/liter.
Curve 5. As 1, but 4.5 ml stabilizing solution/liter.
Curve 6. As 1, but 10.0 ml stabilizing solution/liter.

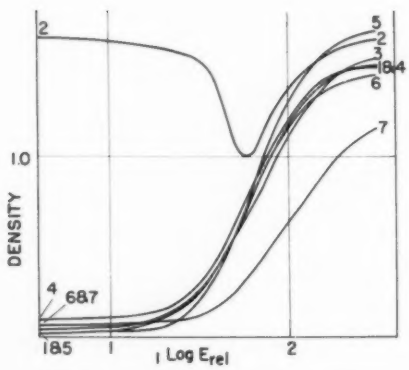


Fig. 6. Effect of contaminating the developer by adding thiourea stabilizing solution and effect of adding potassium bromide. Halobrome paper, Grade 3.

Curve 1. Processing sequence: D-72 (2 min); SB-1; thiourea stabilizing solution.
Curve 2. As 1, but with 0.5 ml stabilizing solution added per liter of developer.
Curve 3. As 1, but with 4.5 ml stabilizing solution and 4.4 grams KBr added per liter of developer.
Curve 4. As 1, but 10.0 ml stabilizing solution and 4.4 grams KBr/-liter.
Curve 5. Processing sequence: Amidol (1 min); $NaHSO_3$ stop solution; thiourea stabilizing solution.
Curve 6. As 5, but 4.5 ml stabilizing solution/liter developer.
Curve 7. As 5, but 10.0 ml stabilizing solution/liter.

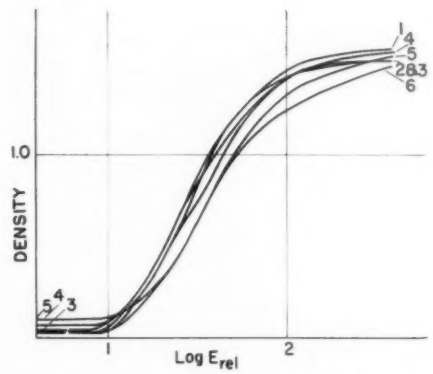


Fig. 7. Effect of contaminating the developer by adding ethylenethiourea stabilizing solution to it. Varigam paper (water-resistant base).

Curve 1. Processing sequence: D-72 (2 min); SB-1; ethylenethiourea stabilizing solution.
Curve 2. As 1, but with 0.5 ml stabilizing solution added per liter of developer.
Curve 3. As 1, but 1.5 ml stabilizing solution/liter.
Curve 4. As 1, but 4.5 ml stabilizing solution/liter.
Curve 5. As 1, but 10.0 ml stabilizing solution/liter.
Curve 6. As 1, except only 1 min development.

the extinction at the maximum absorption decreases from 100% to about 94% in the 0.1 *M* NaOH.)

For practical purposes, however, other properties have to be considered also. They are summed up in Table II as "fixing characteristics." From this information, most of the listed compounds may be ruled out as stabilizers. The fixing time with trimethylthiourea (Compound 7) can be considerably reduced by using more concentrated solutions at elevated temperatures, but then the film remains moist (hygroscopic). More detailed experiments were restricted, therefore, to ethylenethiourea (Compound 5). Though the solubility of $AgNO_3$-(thiourea derivative) compound has no apparent relation to the fixing rate, it may be noticed that all thiourea derivatives of symmetric configuration (Compounds 1,4,5,6) form only slightly soluble silver compounds, whereas those with asymmetrically substituted thiourea (Compounds 2,3,7) are readily soluble. Again the tetramethylthiourea, the silver compound of which is very soluble, is an exception; the corresponding bromide (of the tetramethylthiourea silver complex as compared with the nitrate of this complex), however, is practically insoluble.

Stabilization with Ethylenethiourea

Film: Kodak Super Tri-X film can be stabilized with ethylene thiourea (Compound 5, Table II), but fixing is too slow (8 min). This may be partly due to the lower solubility of this derivative, because a saturated solution (at room temperature) is only half the concentration of the unsubstituted thiourea solution used for stabilizing film.

Paper: Photographic paper can be stabilized with ethylenethiourea within the usual time (1 min). The silver complex of this compound being stable in alkaline solution, a contamination of the alkaline developer (D-72) by the stabilizer is nearly without effect on Varigam (Fig. 7) as well as on Halobrome paper. The disadvantage is an increased fading, which is not only shown by a humidity test (nearly 100% RH for seven days at room temperature) (Fig. 8), but also by drying at elevated temperatures.

Drying by infrared (Fig. 9), which is only feasible for Varigam (because it has a water-resistant base), reduces fading considerably, compared with the usual drum drying at 200° F (Figs. 9 and 10).

The Problem of Fading[8]

The stabilized image, if exposed to high humidity and high temperature, tends to fade by the combined action of aerial oxygen and thiourea. This is not a serious problem for film at room temperature. After standard processing and stabilization, film was kept for one week at nearly 100% RH. A decrease in density was detectable only in the shoulder of the characteristic curve. Fading of paper, however, is much more critical. At room temperature (21° C) and 50% RH there is no fading with stabilized photographic paper, but at 100% RH for one week, fading of both Varigam and Halobrome paper is apparent (Figs. 8 and 11). The latter is somewhat more affected, because the untreated paper base is soaked with thiourea. Amidol developer and sodium bisulfite stop bath favor fading, especially with Halobrome paper, probably because these compounds tend to autooxidize.

The silver developed by D-72 or amidol shows no difference in reactivity towards oxidants (e.g., potassium persulfate + thiourea + acetic acid, aq. soln.). Further experiments were therefore restricted to the D-72 developer and SB-1 (acetic acid) stop bath.

Varigam treated with D-72/SB-1/thiourea showed no fading, and Halobrome, with the same treatment, showed only slight fading during drum drying at 200° F for 3 min.

Prevention of Fading

The following procedure was used in all experiments on methods of improving the keeping quality of stabilized prints:

To eliminate effects of traces of developer residues, the papers, after development by D-72, were stopped with SB-1, fixed with hypo, and washed for 1 hr in running water. The papers were then bathed in diluted acetic acid (SB-1), transferred to the usual thiourea stabilizing bath to which the compound to be tested was added, and finally dried for 3 min at 200° F on a drum drier.

(*a*) *Antioxidants:* Certain phenols and amines, useful as antioxidants in fat and rubber products, are not or are only slightly effective in stopping fading, as shown by the following examples:

Resorcinol	+	*o*-tert.butylphenol	=
Pyrocatechol	=	Hydroxylamine·HCl	=
Tetrachlorohydroquinone	=	Ethylenediamine	=
Hydroquinone	−	Tetraethylenepentamine	+

Key: +, slightly improved; =, unchanged; −, deteriorated.

Other reducing agents, such as ascorbic acid, oxalic acid, hydrazinesulfate, and Phenidone, show a considerable deteriorating effect (− −), probably because such compounds, which are known to form a redox system (e.g., ascorbic acid), can very easily transfer the oxygen from the air to oxidizable matter. Sodium bisulfite is not quite as bad (−).

(*b*) *Compounds that Are Strongly Adsorbed to Metallic Silver:* Because metallic silver is positively charged in spite of the low Ag^+ concentration, preferably negatively charged ions or dipoles should be adsorbed, but the gelatin as well as such compounds as sodium polyphosphate or polyvinyl pyrrolidone show no effect.

(*c*) *Chemicals that Will Form Nearly Insoluble Compounds with Metallic Silver:* Thiosulfate and selenosulfate, because of the easy decomposition of $H_2S_2O_3$ or H_2SSeO_3, release S or Se respectively and form Ag_2S or Ag_2Se. The reaction products, which

8. H. D. Russell, E. C. Yackel, and J. S. Bruce, *PSA Jour.* (*Phot. Sci. & Tech.*), **16B**:59 (1950).

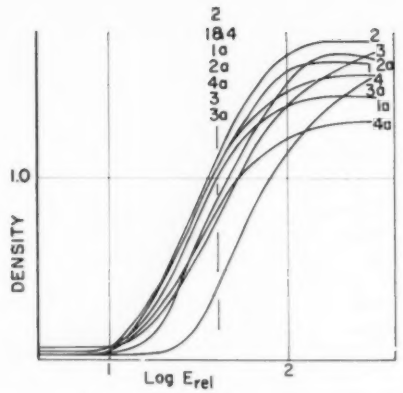


Fig. 8. Effect of high humidity on stabilized prints. Varigam paper (water-resistant base).

Curve 1. Processing sequence: D-72 (2 min); SB-1; hypo; washing.
Curve 1a. As 1, but kept 7 days at 100% RH, 70°F.
Curve 2. Processing sequence: D-72 (2 min); SB-1; thiourea stabilizing solution.
Curve 2a. As 2, but kept 7 days at 100% RH, 70°F.
Curve 3. Processing sequence: Amidol (1 min); $NaHSO_3$ stop solution; thiourea stabilizing solution.
Curve 3a. As 3, but kept 7 days at 100% RH, 70°F.
Curve 4. Processing sequence: D-72 (2 min); SB-1; ethylenethiourea stabilizing solution.
Curve 4a. As 4, but kept 7 days at 100% RH, 70°F.

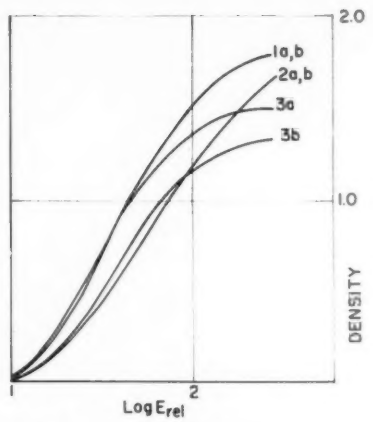


Fig. 9. Effect of drying process on stabilized prints. Varigam paper (water-resistant base). "a" curves, infrared drier; "b" curves, drum drier.

Curves 1a, 1b. Processing sequence: D-72 (2 min); SB-1; thiourea stabilizing solution.
Curves 2a, 2b. Amidol (1 min); $NaHSO_3$ stop solution; thiourea stabilizing solution.
Curves 3a, 3b. D-72 (2 min); SB-1; ethylenethiourea stabilizing solution.

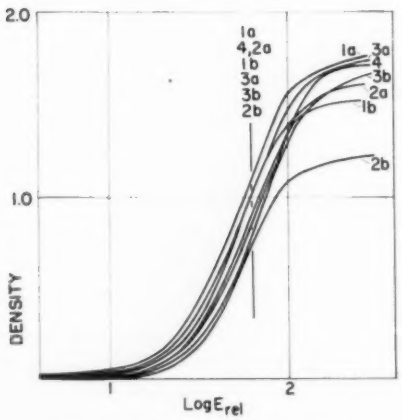


Fig. 10. Effect of drying process on stabilized prints. Halobrome paper, Grade 3. "a" curves, air drier; "b" curves, drum drier.

Curves 1a, 1b. Processing sequence: D-72 (2 min); SB-1; thiourea stabilizing solution.
Curves 2a, 2b. D-72 (2 min); SB-1; ethylenethiourea stabilizing solution.
Curves 3a, 3b. Amidol (1 min); $NaHSO_3$ stop solution; thiourea stabilizing solution.
Curve 4. D-72 (2 min); SB-1; hypo; wash; drum dryer.

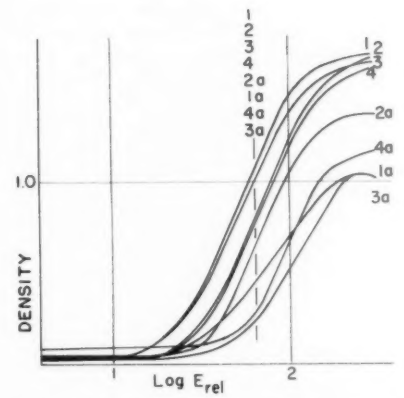


Fig. 11. Effect of high humidity on stabilized prints. Halobrome paper, Grade 3.

Curve 1. Processing sequence: D-72 (2 min); $NaHSO_3$; thiourea stabilizing solution.
Curve 1a. As 1, but kept 7 days at 100% RH, 70°F.
Curve 2. D-72 (2 min); SB-1; thiourea stabilizing solution.
Curve 2a. As 2, but kept 7 days at 100% RH, 70°F.
Curve 3. Amidol; $NaHSO_3$ solution; thiourea solution.
Curve 3a. As 3, but kept 7 days at 100% RH, 70°F.
Curve 4. Amidol; SB-1; thiourea solution.
Curve 4a. As 4, but kept 7 days at 100% RH, 70°F.

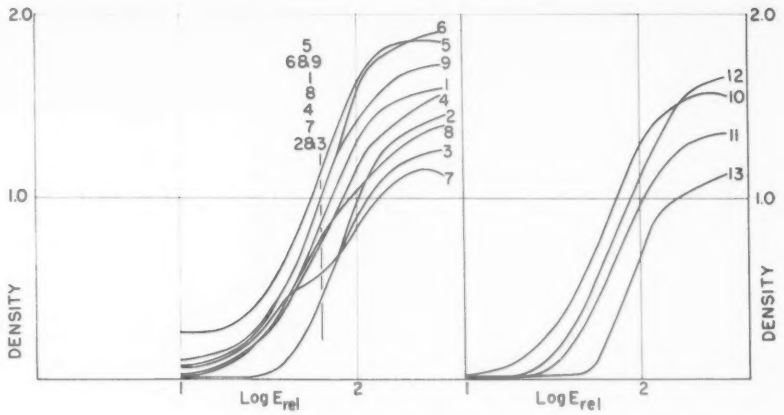


Fig. 12. Effect of 100% RH for 7 days at 70°F on prints on Halobrome paper, Grade 3, processed in the sequence: D-72 (2 min); SB-1; hypo; wash; then treated in the sequence listed for the various curves. All except Curve 6 drum dried.

Curve 1. Without further treatment.
Curve 2. SB-1; thiourea stabilizing solution.
Curve 3. SB-1; thiourea stabilizing solution containing 0.05 M $NaHSO_3$.
Curve 4. SB-1; thiourea stabilizing solution with 0.25 grams/liter $H(AuCl_4) \cdot 4H_2O$ added.
Curve 5. $NaHSO_3$; 0.8 volume thiourea stabilizing solution + 0.2 volume Na_2SSeO_3* solution + 3.2 grams thiourea/liter.
Curve 6. As 5, except air dried.
Curve 7. Na_2SSeO_3; 1 volume thiourea stabilizing solution 0.0016 volume Na_2SSeO_3 solution.
Curve 8. As 7, but 1:0.008 volume ratio.
Curve 9. As 7, but 1:0.032 volume ratio.
Curve 10. As 1.
Curve 11. As 2.
Curve 12. SB-1; thiourea stabilizing solution containing 0.05 M hypo.
Curve 13. SB-1; thiourea stabilizing solution containing 0.05 M oxalic acid.

* The Na_2SSeO_3 was prepared from 3 grams red selenium + 20 grams Na_2SO_3 + 100 ml water; filtered after boiling.

are nearly insoluble, cover the silver as a protective layer. Thiosulfate offers some protection, and the action of selenosulfate is quite strong (Fig. 12). At high humidity, a slight reddish discoloration of the paper develops.

(*d*) *Plating the Surface of the Silver Grain with Nobler Metals:* Gold chloride, which is converted into the corresponding thiourea gold complex by the stabilizing solution, completely overcomes fading (Fig. 12) (gold toning after H. Kessler; also, see Ref. 9). The gamma is slightly lower.

A Possible Intermediate in the Fading Reaction and Its Use as a Powerful Bleaching Agent

The oxidation of thiourea to $(thiourea)_2^{++}$ (short for $(H_2N)_2C{-}S{-}S{-}C(NH_2)_2^{++}$) by hydrogen peroxide suggests that this compound might be formed as an intermediate in the oxidation of silver by oxygen and thiourea. The formation of $(thiourea)_2^{++}$ may occur by reaction of an intermediate, Ag_2O_2, or only by the catalytic action of silver. Further experiments with $(thiourea)_2^{++}$ (the bromide was used) showed that in combination with excess thiourea it is a very powerful oxidizing agent for silver. A solution which is half saturated with $(thiourea)_2^{++}$ and thiourea bleaches a silver image (on paper, density 1.5) within 10 sec, which corresponds approximately to the activity of 30% HNO_3. A gold-toned silver image is bleached at least as readily as a pure silver image. Because a gold-toned image stabilized with thiourea shows no fading, it can be concluded that gold forms no intermediate peroxide or is catalytically inactive.

The role which reducing agents may play in transfering oxygen from the air is demonstrated by the following experiment: A solution of $Na_2S_2O_4$, thiourea, and KBr bleaches a silver image (on Halobrome paper, density 1.5) within 8 min. When shaken with air, it is bleached within 1.5 min.

Solutions of $(thiourea)_2^{++}$ have poor keeping qualities (after several hours a precipitation of sulfur will start), but can be made stable by adding large amounts of KBr if the solution is left in contact with a crystalline precipitate (a mixture of KBr and $(thiourea)_2Br_2$). Such solutions bleach a silver image (density 1.5 on Halobrome paper) within 5 to 30 sec. They could be used for a combined bleaching and fixing bath, but they are acid and, if used for a color process, could affect the dyes.

Buffering (pH 6) of this solution results in precipitation of sulfur. The corresponding derivatives of ethylenethiourea and tetramethylthiourea are much more stable, even in alkaline solution. Both show bleaching times from 1.5 to 2 min in combination with the corresponding mother compound. The combination with thiourea shows bleaching times from 15 to 30 sec, but is not quite stable (slow precipitation of sulfur). The combination with KCNS is more advantageous: $(tetramethylthiourea)_2^{++}$ + concentrated KCNS solution bleaches a silver image on Halobrome paper (density 1.5) within 1 min, and on film (Super Tri-X, density 1.0) within 2 min. The acid reaction can be buffered with KH_2PO_4-K_2HPO_4 mixture or $(NH_4)_2HPO_4$; (dyes of color film will therefore remain unchanged) and the precipitation of decomposition products of the HCNS will be avoided. To allow the silver salts to diffuse out of the layer, the film must be left in the solution for about 10 min and then washed.

9. H. D. Russell, U.S. Patent 2,453,346, Nov. 9, 1948.

Rapid Stabilization at High Temperature and/or High Thiourea Concentration

The Problem of Stickiness of the Gelatin: For many applications of military photography, a drastic reduction of the total processing time, especially for film, is required. Development time can be reduced to a few seconds without difficulty. Removal of the unexposed silver bromide is a slower process. Since stabilization is not based on the removal of unused silver salt, it offers a good possibility for decreasing the processing time. Rapid stabilization can be achieved by high concentration of the stabilizer, by raising the temperature, or both. In either case, excessive swelling and stickiness of the gelatin results and presents a serious problem.

To counteract these effects, prehardened film can be used, hardening agents can be applied, or stabilizing compounds which will not have these harmful effects can be sought; or alcoholic instead of aqueous solutions or saturated aqueous solutions might be used. With some of these methods, reticulation may occur.

The stickiness is probably caused by destruction of the three-dimensional network of the gelled gelatin, which is built up by polypeptide chains, linked together by hydrogen bonds. The separated polypeptide chains then are responsible for the stickiness. The situation is analogous to the difference between vulcanized and unvulcanized rubber. N—H bonds, as well as mercaptide configurations of the stabilizer, seem to be responsible for this effect, preferably establishing intramolecular instead of intermolecular bonds, but this might depend on concentration.

Molecules with numerous functional groups might be expected to reestablish bonds between the polypeptide chain molecules, but at least such polymers as metaphosphate, polyvinyl pyrrolidone, polyvinyl alcohol, carboxymethylcellulose, and carrageenin, are ineffective.

Stabilization at Elevated Temperature: Samples were treated at 120° F with the formulations given in Table I. The developer and stop bath were kept at room temperature. Regular as well as prehardened (Tri-X) film cleared in no more than 25 sec, while for paper 5 sec were sufficient. The short stop cannot be omitted. Without it the fog on film increases to $D = 1.0$ even if the stabilizing solution contains up to 4% KBr. An immersion of film for 5 sec and of regular paper (Halobrome) for 10 sec in the short stop is sufficient, however, to prevent fog.

Before becoming completely dry, the gelatin on the film (to some degree even on prehardened film) tends to become sticky. The stickiness of the gelatin is less pronounced on paper. The situation can be improved by adding to the short stop either formaldehyde (150 ml of 37% solution/liter) or alum (30 grams/liter); chrome alum has no advantage. A slight stickiness remains, nevertheless. Derivatives of formaldehyde, such as hexamethylenetetramine, are not effective.

Ethylenethiourea and some methyl derivatives do not have the adverse effect on gelatin but have other shortcomings, especially an increase in fixing time (see Table II). With symmetric dimethylthiourea (Compound 4, Table II) and trimethylthiourea (Compound 7, Table II) at higher concentrations, the fixing time is nearly as short as with thiourea at the usual low concentration, but the gelatin layer remains moist, probably because of the hygroscopic nature of these derivatives. Moreover, the silver complex salt of symmetric dimethylthiourea decomposes readily in alkaline solution; the corresponding salt of trimethylthiourea is relatively stable. In Table III, the softening action of some thiourea derivatives and some other sulfur compounds is given in arbitrary units: 0 = not sticky; 1 = slightly sticky; 2 = sticky; 3 = very sticky.

TABLE III

(1) Thiourea	2	(8) Tetramethylthiourea	0
(2) Monomethylthiourea	2	(9) Thiosemicarbazide	1
(3) Asymmetric dimethylthiourea	1	(10) Acetylthiourea	0
(4) Symmetric dimethylthiourea	1	(11) Cysteine	0
(5) Ethylenethiourea	1	(12) Thiomalic acid	2
(6) Propylenethiourea	1	(13) Thiosalicylic acid	3
(7) Trimethylthiourea	0	(14) Hypo	1
		(15) Potassium thiocyanate	3

Procedure: Wet film (regular Super Tri-X) is immersed in 0.2 mol. stabilizing solution at 120°F for 30 sec.

Thiourea derivatives such as $H_2N—CS—NH—(CH_2—NH—CS—NH—)_nCH_2—NH—CS—NH_2$ ($n = 0,1,\ldots$) (water-soluble formaldehyde thiourea condensation products) show no softening effect; their stabilizing characteristics are comparable to those of thiourea.

Stabilization at Room Temperature with Higher Concentration of Stabilizer: With saturated thiourea solutions (10% + 1% glycerine), prehardened Super Tri-X film can be stabilized within 15 sec (i.e., the film clears on drying). Moreover, it is possible to process without a stop bath. Some acetic acid (10 ml/liter of stabilizer) will improve the results. The gelatin layer will be only slightly sticky. At room temperature and 50% RH, the image keeps relatively well, but at 100% RH, considerable fading occurs which cannot be prevented even by adding gold chloride to the stabilizing bath.

For some applications, it is desirable to get a transparent image as fast as possible. The following system, using potassium iodide solution, may be used, but it is not superior to the foregoing: A 20% solution of potassium iodide with 1.5% glycerine will stabilize film within 15 sec. A short stop is required (15 sec in SB-1). The film will be somewhat sticky before it becomes completely dry. After

drying, it will be clear and keep relatively well at room temperature, and 50% RH, but at 100% RH there is strong fading which cannot be prevented by adding gold salts to the stabilizing solution.

With concentrated potassium iodide solution, film becomes clear within a few seconds; the gelatin layer, however, swells excessively, and, after it has dried, potassium iodide crystallizes on its surface. Concentrated potassium thiocyanate solution clears just as quickly, but the effect on the gelatin is even more adverse.

Stabilization at High Temperatures with Concentrated Solutions: Clearing time should be the fastest at high temperatures with concentrated solutions. Moreover, the gelatin should not swell in highly concentrated solutions. This is true for thiourea, as shown in Table IV.

TABLE IV

Temperature, deg C	Clearing time, sec	Effect on gelatin
95	2	Not sticky
80	3	" "
65	3	" "
55	4	" "
40	11	Slightly sticky

In the tests from which the data in Table IV are reported, the solution was saturated at each temperature. Prehardened Super Tri-X film was used. After the film dried, some thiourea crystallized on the surface; this can be prevented by a short rinse after the stabilizing bath. One of the operational systems in which rapid stabilization is required calls for the processing of film for immediate image scanning and transmission. In this use, no rinse is needed, because the film emerges quite clear from the stabilizing bath and can be scanned at this stage. Crystallization occurs only after drying. Since the crystals have no adverse effect on the film, at least not within several hours or days, the film can be dried completely after scanning and rinsed later.

On film that is not prehardened, some reticulation will occur. Concentrated potassium thiocyanate solutions, too, cause some reticulation, but there is reticulation even with prehardened film, in contrast to the results obtained at lower concentrations, where excessive swelling of the gelatin occurs.

The use of alcoholic solutions of thiourea to prevent swelling of the gelatin slows down the rate of clearing considerably; moreover, the film base can be affected by the alcohol.

Conclusions

(*a*) Stabilization with thiourea can be practiced in combination with alkaline developer. No precautions are required for film processing; an increase of the potassium bromide content is required for paper processing.

(*b*) Stabilization with thiourea derivatives, although effective in some respects, offers little advantage over-all, because of longer clearing time of the film and increased fading of paper.

(*c*) Several methods for reducing fading are known, the most effective of which were found to be selenium and gold toning.

(*d*) As a result of a study of the fading process, a powerful bleaching bath was found, consisting essentially of an oxidation product of thiourea or one of its derivatives.

(*e*) It is possible to process prehardened film under conditions of high temperature and high thiourea concentration without excessive swelling of the gelatin, thus reducing the time for clearing the film at 95° C to 2 sec.

Acknowledgment

The author is indebted to Dr. Karl G. Leistner, Chief of the Photographic Research Section, USASRDL, and Miss Marilyn Levy for valuable advice and discussions.

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Print-Out Emulsion with a Component of Silver Azide

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Print-out emulsions have been prepared in which part of the silver bromide has been replaced by silver azide. The effects of variation in the silver azide content, of the addition of oxalic acid, and of the addition of excess silver nitrate on the print-out sensitivity have been determined. A formulation is given for a print-out emulsion of improved speed which can be used for the detection and dosimetry of radiation from radio isotopes.

In the usual formulation of print-out emulsions, silver chloride or silver bromide is dispersed with citric acid to make gelatin emulsions in which the presence of excess silver ion facilitates formation of a print-out image. For the present studies, emulsions were prepared with silver bromide in which a part of the silver salt was replaced by silver azide and, moreover, addition of oxalic acid was an important factor in obtaining print-out emulsions of high sensitivity.

Experimental Procedure

The print-out emulsion containing silver bromide and silver azide is formulated as follows:

1.	Gelatin	4	grams
	Water	30	cc
2.	Potassium bromide	2.7	grams (0.023 mole)
	Sodium azide	0.3	gram (0.005 mole)
	Water	20	cc
3.	Silver nitrate	4.5	grams (0.027 mole)
	Water	10	cc
4.	Oxalic acid, 10% solution	3	cc

Solutions 2 and 3 are added simultaneously, with stirring, to Solution 1 at 60°C in 7 min and then Solution 4 is added. The emulsion is coated quickly on a glass plate and cooled, then washed with pure water and, after 2 min bathing in alcohol, dried quickly.

To determine the sensitivity of the emulsions, an optical wedge for sensitometric use is placed in front of a test strip and exposure is made with a 500-w tungsten lamp having an intensity of 1482 candles (color temperature, 3000°K) for 60 sec at a distance of 25 cm from the light source. The density of the print-out image is measured directly by an Ansco Densitometer of the transmission type and characteristic curves are plotted in the ordinary way.

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The densities in the figures represent the increase in density caused by the print-out silver. The original density of the unexposed silver azide emulsion (without silver bromide) of Fig. 1 was 0.70 to 0.75 in terms of transmission density. Similarly, the density of the unexposed silver bromide emulsions containing silver azide (Figs. 2–7) was 0.97 to 1.05.

Emulsion Characteristics and Experimental Results

The formulation of the print-out emulsion used in the present studies is based on the fact that the print-out sensitivity of a pure silver azide gelatin emulsion can be greatly increased by the addition of oxalic acid. Characteristic curves of print-out emulsions of several types are shown in Fig. 1, where the pure silver azide emulsion has extremely low sensitivity and the addition of oxalic acid increases its sensitivity more than 100 times.

A silver bromide emulsion containing citric acid and excess silver ion showed higher sensitivity than the silver azide-oxalic acid system, and finally a silver bromide-silver azide-oxalic acid emulsion of the formula given (see Experimental Procedure) showed the highest print-out sensitivity.

In the silver bromide print-out emulsion containing silver azide, the print-out sensitivity depends largely upon its azide content. Figure 2 shows characteristics of emulsions having various silver

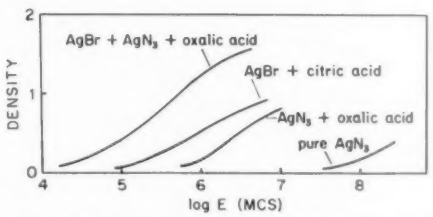

Fig. 1. Characteristic curves of several types of print-out emulsions.

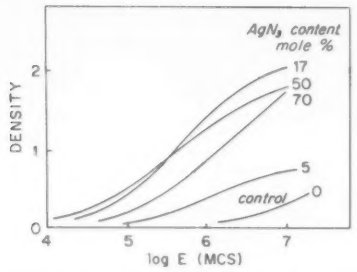

Fig. 2. Influence of silver azide content on emulsion characteristics.

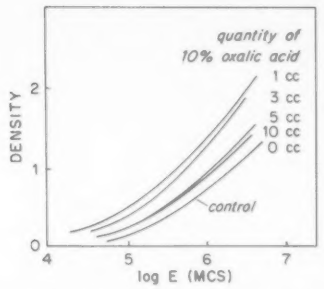

Fig. 3. Influence of oxalic acid on emulsion characteristics.

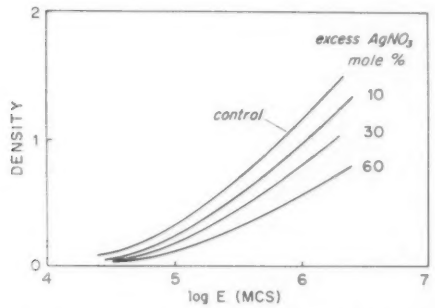

Fig. 4. Influence of addition of excess silver nitrate to the emulsion.

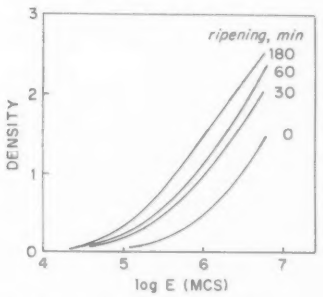

Fig. 5. Increase of print-out sensitivity by ripening.

azide content where the ratio of sodium azide to potassium bromide is varied in the formula given (see Experimental Procedure). Thus a silver azide content of 17 mole % results in the highest densities, with near maximum sensitivity.

Characteristic curves of the silver bromide-silver azide print-out emulsions with various quantities of oxalic acid are shown in Fig. 3, and here the greater the quantity of 10% oxalic acid solution added the lower the print-out sensitivity. Figure 4 shows the influence of the addition of excess silver nitrate to the silver bromide-silver azide emulsion. Thus, the addition of excess silver nitrate leads to a decrease of print-out sensitivity.

The results shown in Fig. 4 were obtained when the silver nitrate was added in the final step of emulsion making (before coating and washing). When silver nitrate was added before the oxalic acid solution, the decrease in sensitivity was not so large. This suggests that the addition of excess silver nitrate in the final step dissolves (slightly) the silver azide or silver oxalate, either of which would sensitize the print-out effect.

It is noticeable that the print-out sensitivity of the silver bromide-silver azide emulsion in these experiments can be increased by ripening. Figure 5 shows the effect of ripening at 60° C for various periods, for an emulsion prepared with an inert type of gelatin. Two emulsions prepared by the same formula, but one with an inert type (PH-28) and the other with an active type (RF-19-3) of gelatin, showed the same ripening effect (see Fig. 6).

Finally, the sensitivity measurements were extended to gamma radiation, using a radioisotope, cobalt-60, as a gamma-ray source having a dose rate of about 5×10^4 r/hr. In this case, irradiation was made by the time-scale method from 30 min to 15 hr. In the right-hand chart, Fig. 7, the print-out density curve of the silver bromide-silver azide emulsion is compared with that of silver bromide emulsion. The curves in the left-hand chart, Fig. 7, show the sensitization by ripening for the silver bromide-silver azide print-out emulsion of the formula given. Without ripening, the print-out image appears upon irradiation of the order of 10^5 to 10^6 roentgens and the sensitivity is markedly improved by ripening. The emulsion ripened for 180 min shows a print-out density of 0.35 for gamma-ray irradiation of 3×10^4 roentgens.

Discussion

The print-out emulsion used in the present studies is composed of silver bromide, silver azide, and oxalic acid; excess silver ion is not needed. On the contrary, it is observed that the presence of excess silver ion leads to a decrease of print-out sensitivity. The mechanism of print-out image formation in the emulsion without excess silver ion must be somewhat different from that discussed for silver halide emulsions containing citric acid and excess silver ion.[1] If there is no excess silver ion in an emulsion, as in

1. B. Fergg, *Z. wiss. Phot.*, **52**: 24 (1957).

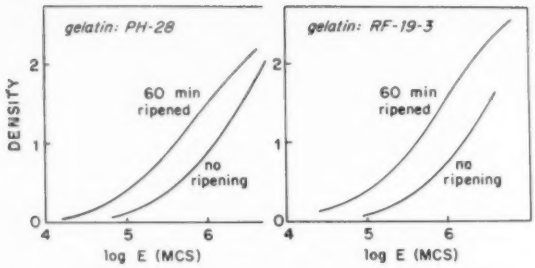

Fig. 6. Influence of ripening on emulsions with two types of gelatins

these studies, addition of oxalic acid does not result in silver oxalate formation, and so the role of the organic acid must be considered from another standpoint.

Now, it is demonstrated by another experiment that the same type of print-out emulsion can be prepared by making use of formic acid in place of oxalic acid, although the emulsion containing formic acid is not so stable. It may be reasonable to assume that the reducing action of these organic acids may act to form silver atoms in the crystal grains in the emulsion, and the reduced silver atoms must play an important role in the formation of print-out image. Moreover, the fact that addition of oxalic acid to a pure silver azide emulsion greatly enhances the print-out phenomenon (see Fig. 1) suggests that oxalic acid reacts easily with silver azide, leading to the formation of silver atoms. This reaction may occur also in emulsions in which the silver bromide is partially replaced by silver azide, making a favorable condition for print-out image formation with three components, silver bromide, silver azide, and oxalic acid.

Use of print-out emulsions for radiation detection or dosimetry of high-energy radiation is described by H. F. Nitka,[2,3] who points out that commercial print-out-paper emulsions are quite useful for radiation dosimetry. H. T. Dybvig[4] has also studied high-speed print-out emulsions for this purpose. The emulsion used in the present studies is available for gamma-ray radiation dosimetry where dosage can be determined by a simple method which does not require processing.

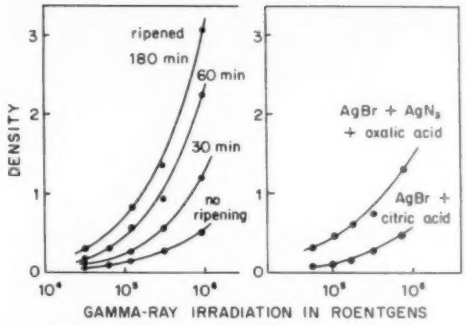

Fig. 7. Gamma-ray sensitivity of print-out emulsions, showing the effect of ripening.

Conclusion

A print-out emulsion is prepared with silver bromide in which a part of the silver salt is replaced by silver azide in the presence of oxalic acid. This type of print-out emulsion does not contain excess silver ion and the mechanism of print-out image formation may be different from that of ordinary emulsions. The print-out emulsion is sensitive to gamma rays of cobalt-60 in the irradiation region of over 10^4 roentgens and is applicable to dosimetry of high-energy radiation.

2. H. F. Nitka and D. P. Jones, *Nucleonics*, **15**: (10) 128 (1957).
3. H. F. Nitka, *ibid.*, **17**: (10) 58 (1959).
4. H. T. Dybvig and T. R. Thompson, *Phot. Eng.*, **5**: 127 (1954).

PHOTOGRAPHIC SCIENCE AND ENGINEERING
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Electrothermography—A New Electrostatic Printing Technique

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A process has been developed by which electrostatic prints can be obtained by heat dissipation of an applied charge. The method is based on a spontaneous discharge at a critical temperature. A tentative explanation of the phenomena involved is offered and is supported by resistivity, enthalpy, and breakdown measurements.

Since Carlson's original patent on xerography,[1] several techniques have been described by which an electrostatic charge is applied to a semiconductor and a print is produced by an imagewise dissipation of the charge.[2] The decay of the charge is always caused by radiation. Incident photons excite active centers of the semiconductor crystal, thereby creating free charge carriers. These carriers are raised to the conduction band, and move through the crystal lattice, finally dissipating the original charge.

Heat Decay of the Electrostatic Charge

The purpose of the present paper is to discuss the possibility of obtaining an electrostatic print by imagewise dissipation of the charge by heat rather than by light. The basic mechanism of such a technique, which for convenience will be called electrothermography, is compared to electrophotography in Fig. 1.

Consider a layer of a dielectric material onto which an electrostatic charge is applied. An original piece of copy, bearing radiation-absorbent characters on white background, is brought into close contact with the dielectric surface, and a brief but intense exposure is made through either the original or the dielectric base. During exposure, radiation is absorbed in the characters and converted to heat. Heat waves originating from each character raise the temperature of the corresponding spots of the dielectric, thereby lowering its resistivity. The heated spots of the dielectric lose their original charge, and a charge pattern closely similar to the original density pattern will result. By dusting this charge matrix with an electroscopic powder, a facsimile is obtained.

The very fact that heating of a dielectric lowers its resistivity is not very surprising, since many dielectrics as well as semiconductors have negative temperature coefficients. However, in order to record an image by heat dissipation of an electrostatic charge, a critical point should be considered.

In practically any original, the incident radiation is neither quantitatively absorbed by the characters, nor fully reflected or transmitted by the background. Actually, only a relatively small temperature difference will exist between image and background, ranging from 5° to 20°C for most originals.

The charge decay-vs-temperature curves of two typical semiconductors are shown schematically in Fig. 2. Semiconductor A exhibits a continuous decay, whereas the curve of Semiconductor B shows a break at a critical temperature. In Curve A, a difference in temperature of 5°C, corresponding to the temperature difference between image and background, produces too small a difference in residual charge, not detectable by ordinary developing methods. The resulting print will have poor contrast. In Curve B, however, a substantial lowering of the resistivity occurs beyond the break point. In recording an image with this semiconductor, the exposure is so controlled that the temperature of the background remains well below the break, whereas the temperature of the image parts is raised above the same point. The net difference between both residual charges affords a satisfactory contrast.

Materials suitable for use as image-forming layers in electrothermography were found to be amply available. The charge-vs-temperature relation of a great many products, inorganic as well as organic

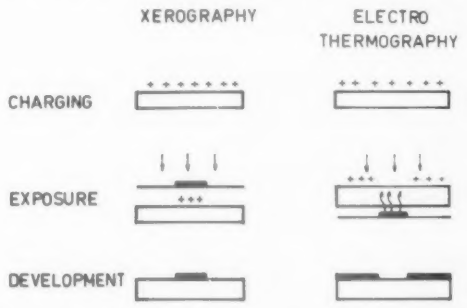

Fig. 1. Electrothermography compared to electrophotography.

Presented at the Annual Conference, Santa Monica, California, 12 May 1960. Received 27 April 1960.

1. C. F. Carlson, U.S. Patent 2,221,776, Sept. 8, 1938.
2. P. M. Cassiers, *Elektrofotografie, Belg. Chem. Ind.*, **XXV**(2): 127 (1960).

and polymeric, exhibit more or less definite breaks at critical temperatures. For practical purposes, a sheet of a thermosensitive insulator or semiconductor is used, bearing on one side an electrically conductive layer. Laminates of polymer film on paper, or polymer sheet material vacuum coated with a metal film of a few hundred Angstroms, were found equally suitable.

Experimental Results

As representative examples of the present process, the performance of two polymers will be discussed.

The first material is a laminate of paper and polyethylene of the high-pressure, branched type. An electrostatic charge is deposited by a corona device onto the polyethylene, and the laminate heated for 1 min at different temperatures, while the charge decay is continuously recorded. The resulting charge temperature characteristic is shown in Fig. 3. From about 50°C on, the charge is slightly lowered, and beyond 70°C a rapid decay takes place.

If the charged laminate is pressed in contact with a heated plate for a few seconds, and after cooling is dusted with black powder, the powder deposit decreases with rising temperature, as shown in Fig. 4. The threshold of the heat image, e.g., the first temperature where the density is visibly lowered, is situated near 50°C. By variation of heating time, control of gradation and sensitivity of the image is possible between certain limits.

For a better understanding of the discontinuous charge decay phenomena, a comparison between the decay characteristic of the present material and other physical properties was attempted. The volume-resistivity-vs-temperature relation of the same polyethylene laminate is recorded in Fig. 5. At about 58°C, a clear break point is observed.

If the enthalpy vs temperature of the polyethylene used in the former experiments is recorded (Fig. 6), a first-order transition is found between 50° and 60°C, marking the beginning of the melting range, which is completed at about 120°C.

Another typical example consists of a foil of cellulose acetate (degree of substitution 2.4) containing 20% of triphenyl phosphate and vacuum coated on one side with aluminium.

The characteristic charge temperature function of this material, shown in Fig. 7, shows a sharp break point near 38°C. The density-temperature relation of the powder image (upper curve, Fig. 7) closely corresponds to the charge decay.

The volume-resistivity curve (Fig. 8) exhibits a discontinuity rather than a break between 30° and 40°C. The enthalpy-vs-temperature graph (Fig. 9) reveals two apparent second-order transitions near 40° and 120°C, the lower one corresponding to the critical points of the other curves.

By volumetric study of cellulose acetate containing 30% of plasticizer, transition temperatures of 37° and 130°C have been found.[3]

Discussion

Any discussion of the aforementioned phenomena involves basic assumptions about the nature, site, and displacement of charge carriers in dielectrics.

An idealized model of the electron band structure in amorphous dielectrics, as proposed by Fröhlich,[4] is supported by Simpson[5] and Fowler.[6] A discontinuous energy level distribution is assumed, which inhibits free movement of low-energy electrons through the dielectric. Since the high resistivity of many polymeric materials would require a number of traps as high as 10^{13} to 10^{20}/cc, an electron may be repeatedly excited and trapped at higher energy levels without actually sustaining conduction. In case of sufficient excitation, as by radiation or by a strong field, the electron at last reaches a state considered equivalent to the conduction band level of a crystal.

If an ionizing corona discharge is applied to a dielectric, an electrostatic charge of the same sign as the polarity of the corona wire is detected on the corona side, and a somewhat smaller countercharge of opposite sign on the reverse side. This "blocking

3. J. Russell and R. G. Van Kerpel, *J. Polymer Sci.*, **25:** 77 (1957).
4. H. Fröhlich, *Proc. Roy. Soc. (London)*, **188A:** 521 (1947).
5. J. H. Simpson, *Proc. Phys. Soc.*, **63A:** 86 (1950).
6. J. F. Fowler, *Proc. Roy. Soc. (London)*, **236A:** 464 (1956).

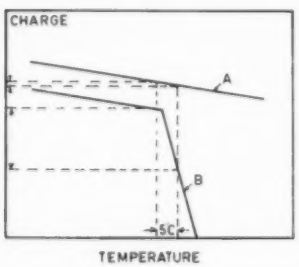

Fig. 2. Schematic charge decay as a function of temperature for two typical semiconductors.

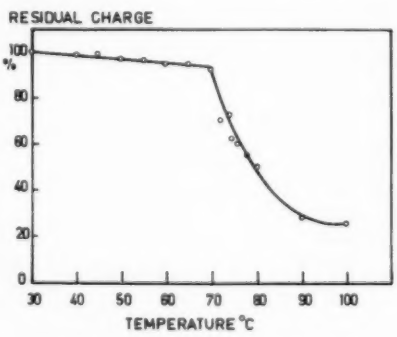

Fig. 3. Residual charge after 1 min at different temperatures—polyethylene paper.

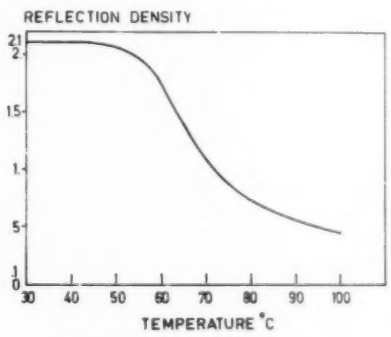

Fig. 4 Powder density of heat image—polyethylene paper.

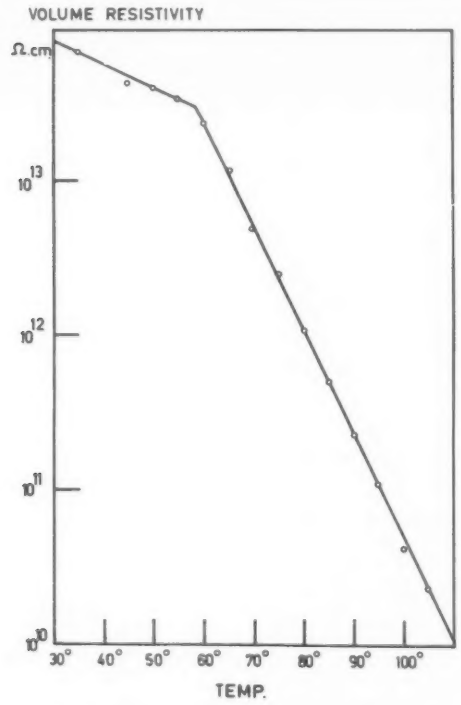

Fig. 5. Resistivity vs temperature—polyethylene paper.

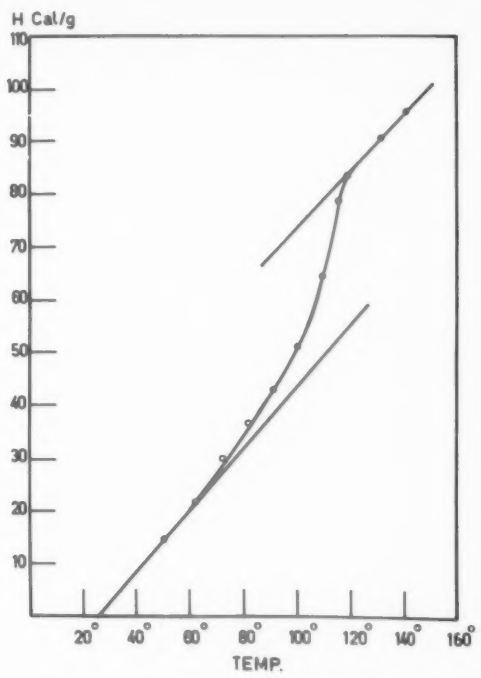

Fig. 6. Enthalpy vs temperature—polyethylene paper.

electrode" consists of charged gas ions.[7] The formation of a polarization charge in deep traps inside the dielectrics, as in so-called photoelectrets[8], need not be considered here, since the latter mechanism produces a heterocharge (of sign opposite to the polarity of the contacting electrode) and decay half times considerably longer than those obtained by corona. The field strength, supported by the charges on both sides of the dielectric, is of the order of 2 kv/cm, and provides an active acceleration of any excited charge carriers in the dielectric.

The nature of the charge carriers involved in dielectric conduction is assumed to be electronic. This assumption is supported by the close similarity between heat decay curves of the polymers discussed here, and light decay curves in inorganic, organic, and polymeric photoconductors. Although ionic conduction in polymers at high temperatures has recently been reported,[9] the mobility of the heavy ionic structure must be considered too slow to explain the observed rapid decay.

A mechanism of dielectric breakdown at the critical temperatures involved has been considered. For both polymers discussed here, however, even at the temperatures corresponding to the charge decay discontinuities, the required breakdown potential is considerably higher (by a factor of at least 100) than the actual charge field strength. The typical perforation of "hot spots" accompanying breakdown has not been observed in the heat decay experiments.

Anomalous conduction at the apparent second-order transition temperature has been reported.[9] For polymethylmethacrylate, a conduction peak as much as 70°C below glassy state transition was observed, and ascribed to twist of the ester groups.

Conclusion

The satisfactory correspondence within the limits of error between spontaneous charge decay temperature and the observed discontinuity in the resistivity and enthalpy curves emphasize the relation between structural changes of the dielectric, such as first- and second-order transitions, and the conduction phenomena. At room temperature, all electrons are in thermal equilibrium under the applied charge field, and are trapped in amply available structure discontinuities. Any increase in temperature below a transition point causes a slight adjustment of the equilibrium in the ratio of electrons in the conduction band to those trapped at shallow levels. Beyond the transition point, structural changes and twists of polar groups (if available) induce a sudden release of trapped electrons, which are raised to the conduction band and accelerated in the existing field, dissipating the original charge.

7. W. Ruppel, H. J. Gerritsen, and A. Rose, *Helv. Phys. Acta*, **30:** 49 (1957).
8. G. Nadjakov, *Physik. Z.*, **39:** 226 (1938).
9. H. V. Herwig and E. Jenckel, *Z. Elektrochem.*, **63:** 360 (1959).

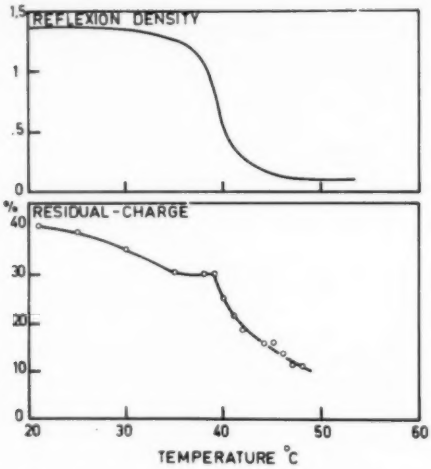

Fig. 7. *Top:* Powder density of heat image—cellulose acetate film. *Bottom:* Residual charge after 1 min at different temperatures—cellulose acetate film.

Applications

One application of the described phenomenon lies in the document-copying field. The present technique allows reflectographic printing of all matter, printed with infrared-absorbing ink. The necessary equipment is similar to existing electrophotographic equipment. Exposure is done with light sources rich in infrared radiation, such as are available in the "Thermc-Fax" printer. Copying time is a matter of seconds.

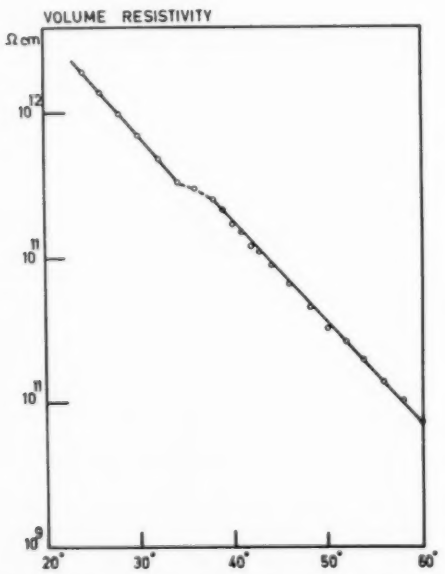

Fig. 8. Resistivity vs temperature—cellulose acetate film.

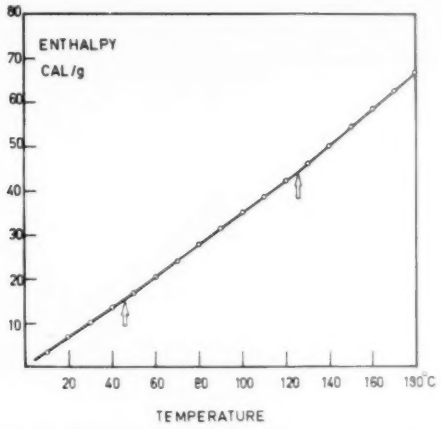

Fig. 9. Enthalpy vs temperature—cellulose acetate film.

Compared to existing thermal copying technique, electrothermographic paper is perfectly stable to light and heat, before as well as after printing. Contrast is similar to that in printed matter, but resolution is relatively low. Positive and negative copies may be obtained at will by the simple choice of the sign either of the applied charge or the developer powder. Prints may be developed in any wanted color and the powder image may be transferred to any likely support such as, e.g., filing-card stock.

Another application of controlled heat discharge of a dielectric is in the field of electrostatic recording. Techniques wherein information is stored as a surface charge on an insulating surface include reproduction of scanned or television images, and memories in analog and digital computers. Quick erasure of the electrostatic signal sometimes is difficult. By choice of a suitable dielectric, heating just beyond one transition point of the material provides a rapid and efficient erasure of the surface charge.

Experimental Procedure

All electric measurements were performed at 21°C and 52% relative air humidity. Electrostatic charges were measured by an electrometer of the vibrating electrode type,[10] with the base plate heated thermostatically. Charge was continuously registered on a Bruehl and Kjaer level recorder. Breakdown tests were made according to DIN No. 53.481.

Acknowledgments

The author is grateful to Mr. Martaux for the performance of the experiments, to Dr. Bisschops for the enthalpy measurements and to Optilux p.v.b.a. for carrying out the metallizing of the cellulose acetate. The author is particularly indebted to Dr. Conix for valuable suggestions leading to this study, and to Mr. Van Kerpel for helpful discussions.

10. C. J. Young and H. G. Greiz, *RCA Rev.*, 15: 469 (1954).

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Volume 4, Number 4, July-August 1960

Measuring and Judging Photographic Exposure of Color Film for Automatic Exposure Controlled Cameras

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The accuracy of an automatic camera in measuring *photometric exposure* is closely controlled in manufacture by precise and reproducible methods. The photographer may decide his exposure preference by comparing several photographs which differ only in exposure. The difference between the predetermined exposure and the *preferred-picture exposure* is the *discrimination accuracy* of the meter. While the discrimination error is not apparent for most scenes, it may be as much as one exposure value unit for some unusual scenes. This paper explains methods of measuring the different types of exposure accuracy and defines the terms.

Correct exposure can be judged from the appearance of a color transparency, although it may be evaluated differently by different people. Each observer thinks the correct exposure is that which he prefers. If different exposures of the same scene are judged by several observers, the one preferred by the majority is called the *preferred-picture exposure*. The exposure that will be preferred cannot be exactly predetermined. It can only be evaluated by human judgment, and different observers may not agree closer than ± 1 Ev (exposure value units).

On the other hand, exposure within ± 0.5 Ev of the *preferred-picture exposure* can usually be predetermined by photometric measurements of a scene quite satisfactorily for most amateur color work. An experienced photographer can often improve the indicated exposure by judging the brightness of the subject in comparison with the general scene conditions measured by the meter, although for many types of scenes, he cannot know in advance the lightness or darkness of the subject matter which will best express the desired mood. Consequently, in important situations, he will make three exposures to bracket the range indicated by the meter.

It is necessary to recognize this fundamental difference between *photometric measurement of exposure* and *preferred-picture judgment of exposure*. One is foresight while the other is hindsight; the former can be precisely measured and expressed in numbers, while the latter can be found only by judging finished pictures. The two are equal for the statistical average scene.

In the manufacture and evaluation of exposure controls, it is necessary to establish specifications of performance based on reproducible test methods. This paper describes the measurement of calibration accuracy, defines the necessary nomenclature, and gives the theoretical formulas for photometric calibration of exposure controls.

Presented at the National Conference, Chicago, 28 October 1959. Received 4 April 1960.

Correct Exposure—Three Types

The exposure accuracy of automatic exposure-controlled cameras can be determined in three ways: (1) by photometric tests of the cameras; (2) by judging pictures made with precision-calibrated cameras; or (3) by similar judgment, using random factory-built cameras. While the statistical average of the results of all three methods should be the same, variations in scene-luminance distributions cause discrepancies up to ± 1 Ev when samplings do not include all types of scenes, subjects, lightings, and judges.

Table I shows a classification of the three methods of measuring accuracy. Each is determined from different pairs of exposure tests. The terms used are defined below:

Standard exposure is the calculated exposure in the focal plane, computed in accordance with the American Standard formulas. The design, manufacture, and calibration of exposure meters and controls are based on this exposure because it can be expressed in numbers with suitable tolerances. The *standard exposure* is intended to be the statistical mean of the *preferred-picture exposures* and the *choice exposures*. Correlation has been good.

Photometric exposure is the exposure in the focal plane measured by photometric laboratory methods in which both the test-camera lens and its light-measuring system are simultaneously exposed to a surface source of uniform luminance.

Calibration accuracy is the difference, expressed in exposure value units, between the *photometric exposure* and the *standard exposure* of a particular camera and for the test conditions used. The error is positive when it corresponds to overexposure, and is

TABLE I — Classification of Accuracy Tests of Automatic Exposure Controlled Cameras

	Exposure			Test Field		Accuracy	
Designation		Formula	Precision	Luminance	Type	Formula	Designation
(1)	Standard	$B_1S/K_1 = 2^{Ev_1}$	± 0.08 *Ev*	B_1	Uniform surface source	$Ev_2 - Ev_1$	Calibration accuracy
	Photometric	$B_1S/K_2 = 2^{Ev_2}$	Being measured				
(2)	Actual	$A_3/T_3 = B_3S/K_1 = 2^{Ev_3}$	± 0.1 *Ev*	B_3	Scene	$Ev_4 - Ev_3$	Discrimination accuracy
	Preferred-picture	$A_4/T_4 = B_3S/K_4 = 2^{Ev_4}$	Observer's judgment				
(3)	Random	$A_5/T_5 = B_5S/K_5 = 2^{Ev_5}$	Within factory tolerance	B_5	Scene	$Ev_6 - Ev_5$	Random discrimination
	Choice	$A_6/T_6 = B_5S/K_6 = 2^{Ev_6}$	Observer's judgment + calibration errors				

B = field luminance
S = ASA film speed
K = exposure meter constant
Ev = exposure value
A = f-number
T = time interval
A_3 and A_4 = actual f-numbers
T_3 and T_4 = effective shutter time intervals
A_5 and A_6 = f-numbers marked on lens
T_5 and T_6 = time intervals marked on shutter

seldom the same at all luminance levels. The calibration accuracy of an exposure meter or control can be precisely and quickly measured in the photometric laboratory and expressed in terms of manufacturing tolerances. It is the only quick and dependable measure of the performance of automatic exposure controls.

Actual exposure is the actual camera exposure used in making a test picture. The *actual exposure* value is computed from laboratory measurements of the actual lens f-number and the effective shutter time interval corresponding to the camera settings used. Preferably, the camera should be calibrated before and after the tests, and the actual film speed of the test film should be ascertained.

Preferred-picture exposure is that preferred by a group of observers from a sequence of different *actual exposures* for a particular scene and lighting.

Discrimination accuracy of an exposure meter or control is the difference, expressed in exposure value units, between the *actual exposure* of an automatic camera and the *preferred-picture exposure*. The error is positive when the *actual exposure* is the greater. The *discrimination accuracy* of an automatic camera is expected to be within the limits given in Table II and illustrated by the graph, Fig. 1.

TABLE II

Per cent of scenes	Maximum discrimination error expected
68	± 0.5 Ev
95	± 1.0 Ev

These differences occur with meters and cameras having perfect calibration.

Most observers will not be aware of the $\pm$ 0.5 Ev variation in the majority of pictures. But those few pictures in the remaining one third of the scenes which deviate up to $\pm$ 1.0 Ev may be recognized as less than perfect. The discrepancies are due to the infinite variety of luminance distribution in scenes, combined with differences in judging conditions and the variation in what different people look for in pictures. Many methods for improving the discrimination of a meter have been tried, but the only one of general usefulness is to minimize the influence of variations in sky luminance.

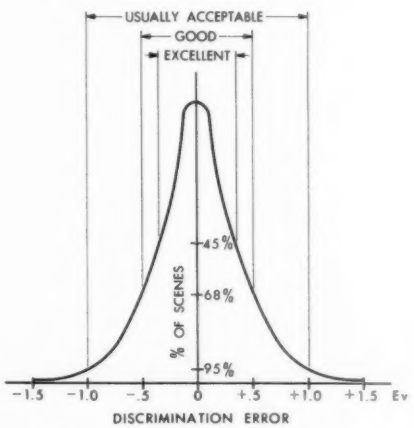

Fig. 1. Discrimination accuracy of automatic exposure controls

Random exposure of a particular camera is the exposure resulting from setting the camera according to the calibration markings on it and using it with random film. All components are expected to be accurate within factory tolerances.

Choice exposure is the exposure which is judged to be the best for a particular scene selected from a sequence of different exposures made according to markings on the camera.

Random discrimination is the difference in Ev units between the *random exposure* and the *choice exposure*. The error is positive when the *random exposure* is the greater.

The many tolerances and uncertainties in exposure control systems add up to an alarming possible error. However, many of the errors are usually opposite in direction and, therefore, are mutually compensating. The *random discrimination* of automatic-exposure controls is surprisingly good compared to technical possibilities.

Standard Exposure Formulas

The well-known American Standard formulas[1] for the camera exposure, A^2/T, measured in terms of the field luminance, B, for a film of sensitivity, S, are as follows:

$$A^2/T = 2^{Ev} = BS/K \qquad (1)$$

where A = actual f-number of lens
T = effective shutter time in seconds
Ev = exposure value
B = field luminance (of a uniform surface source) in footlamberts
S = ASA film speed
K = constant

The selected value of K determines the exposure meter's calibration. The history of the value of K is shown in Table III.

TABLE III

	Maximum	Mean	Minimum
1939 Prewar meter manufacture..	6.3	——	2.5
1944 American War Standard (Jan-M-58)	——	3.93	——
1948 American Standard (Z38.2.6)	4.25	——	3.14
1957 American Standard (PH2.12)	4.25	3.6	3.14

All meter, camera, and film manufacturers had opportunity to participate in, or comment on, the 1957 revision of the American Standard for Exposure Meters. None expressed any desire to change the limiting values of K. The twenty years of experience indicates that 3.6 is a good mean value.

1. American Standard for Photographic Exposure Meters, Photoelectric Type, PH2.12-1957, American Standards Association, 10 E. 40 St., New York 16, N.Y.

Exposure Measured in the Focal Plane

Having established the values of K, the illuminance in the focal plane of the camera can be calculated from the formula[2,3]

$$I = qB/A^2 = 0.223B/A^2 \qquad (2)$$

where I = illuminance in focal plane in footcandles
$q = 0.223$ = constant in lens transmission formula

By combining Eqs. (1) and (2),

$$I = qK/TS = 0.805/TS \qquad (3)$$

The exposure in the focal plane is

$$IT = qK/S = 0.805/S \text{ (footcandle-seconds)} \qquad (4)$$

The numerical values in Eqs. (2), (3), and (4) are derived from the following assumptions:

a. The lens images an infinite surface source of uniform brightness.
b. A modern coated lens is used.
c. Focus is on infinity.
d. Transmission of lens is 95%.
e. Average illumination equals that at 10° off axis.
f. The exposure constant K is unique for all ranges in the American Standard Exposure Formula.[1]

For the same film speed and shutter time, the illuminance in the focal plane of a camera should be constant for all values of scene brightness as long as the relative aperture is varied inversely.

Formulas (2), (3), and (4) are derived from American Standards. The empirical value for lens transmission efficiency was determined by Kodak Research Laboratories. The material has been summarized in papers by Allen Stimson[4] and by C. N. Nelson[3] and is incorporated in the current revision of the American Standard for exposure meters.[2]

Measurement of the exposure in the focal plane is the most accurate way to calibrate a camera. It is better than calibrating the lens in T-stops. All errors of lens aperture, transmission, shutter time, and efficiency are eliminated. When cameras are calibrated by measuring the illuminance in the focal plane, the lens and aperture errors are eliminated.

Focal-Plane Illuminance

Using Formula (3), tables of illuminance in the focal plane have been computed for the usual ranges of time and film speed. A few representative values are given in Table IV. The illuminance in the focal plane (using a single exposure time) must be constant

2. American Standard for Photographic Exposure Meters, Photoelectric Type, PH2.12-1960, American Standards Association, 10 E. 40 St., New York 16, N.Y.

3. C. N. Nelson, *Phot. Sci. and Eng.*, **4**: 48 (1960).

4. *New Developments in Exposure Meter Technique*, presented at the 1946 National Convention, Photographic Society of America, Rochester, N.Y.

TABLE IV — Focal-Plane Illuminance in Footcandles for Standard Exposure (K = 3.6)

Effective time, 1/sec	ASA Film Speed						
	10	32	40	125	160	200	400
4	0.322	0.101	0.080	0.026	0.0201	0.016	0.008
8	0.644	0.201	0.161	0.051	0.040	0.032	0.016
15 (16)	1.29	0.402	0.322	0.103	0.080	0.064	0.032
30 (32)	2.58	0.805	0.644	0.206	0.161	0.129	0.064
40	3.22	1.01	0.805	0.258	0.201	0.161	0.081
60 (64)	5.15	1.61	1.29	0.412	0.322	0.258	0.129
70	5.63	1.76	1.41	0.451	0.352	0.282	0.141
80	6.44	2.01	1.61	0.515	0.402	0.322	0.161
125 (128)	10.3	3.22	2.58	0.824	0.644	0.515	0.258
250 (256)	20.6	6.44	5.15	1.65	1.29	1.03	0.515

TABLE V — Field Luminance in Footlamberts for Standard Exposure (K = 3.6)

ASA Film Speed	Effective time, 1/sec	Actual lens f-number (A)						
		1.9	2.8	4	5.6	8	11	16
10	30 (32)	41.6	92	184	368	737	1470	2950
	40	52.0	115	230	460	920	1840	3680
	80	104.0	230	460	920	1840	3680	7370
32	30 (32)	13.0	28.8	57.6	115	230	460	920
	40	16.2	36.0	72.0	144	288	575	1150
	80	32.5	72.0	144	288	575	1150	2300
160	30 (32)	2.60	5.75	11.5	23.0	46.0	92	184
	40	3.25	7.20	14.4	28.8	57.6	115	230
	80	6.50	14.4	28.8	57.5	115	230	460

for all lens apertures to obtain Standard Exposure of the film.

To measure the focal plane illuminance, the lens and meter are equally exposed to a uniform surface source of luminance, B, computed from Formula (1). The values of luminance for a few conditions are given in Table V.

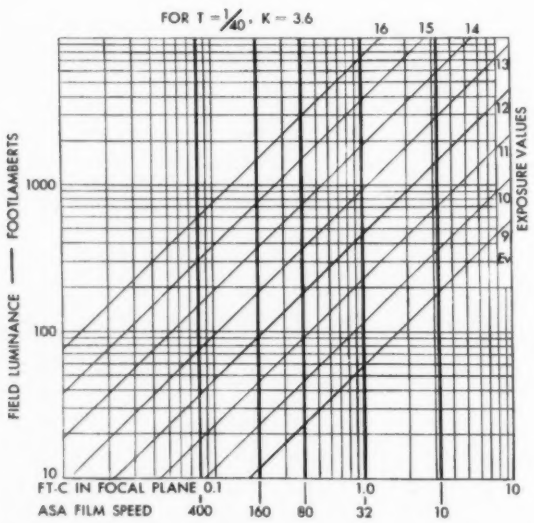

Fig. 2. Calibration chart, automatic exposure controlled cameras.

For a selected combination of time and film speed, the focal-plane illuminance given in Table IV should be constant for all field-luminance values. Table V gives values of field luminance corresponding with the tabular f-number which will result in the *standard exposure* when using the time and film speed shown on the same line.

The accuracy of laboratory illuminance measurements in the focal plane should be within ± 6% or 0.08 Ev.

Test results can be shown graphically as on the diagram in Fig. 2.

Preferred-Picture Exposure

The camera exposure which results in the preferred picture is the objective of every picture taker. The statistical average of *preferred-picture exposures* determines the *standard exposure*. The *preferred-picture exposures* of a selected scene may differ up to ± 1.0 Ev from the *standard exposure* for the equivalent scene luminance. There is always an uncertain relation between particular pictures and the statistical average picture. In best studio practice, exposures can be predetermined within about ± 0.3 Ev of the *preferred-picture exposure*.

Effect of Scene Type

For more than twenty years, meter manufacturers have recognized that certain types of scenes and lightings cause the *preferred-picture exposure* to differ

from the *standard exposure*. These differences have been written into their instruction books and have been described in the literature in hundreds of articles. Here are a few samples:

a. For side-lighted subjects, increase the indicated exposure 0.5 Ev.
b. For back-lighted subjects, increase the indicated exposure by 1.0 Ev.
c. On overcast days, increase the exposure by 1.0 Ev, because the sky, as the only source of light, is relatively brighter compared to foreground objects than on sunny days. Also, the lower lighting contrast permits more exposure without "washing out" highlights and often results in a brighter and a more pleasing picture.
d. In snow and beach scenes which include peoples' faces, increase the exposure 1.0 Ev. On glare, ice, and snow, the correction may be as much as 2 Ev.

In judging a meter's performance from the appearance of the *preferred-picture exposure*, the above types of corrections must be factored into the decisions.

Differences between Judges

It has been found that, in judging a sequence of identical pictures having different exposures, observers may differ in their exposure preference for some types of scenes by as much as 1.0 Ev. They usually disagree most on scenes of lower contrast.

A film may be judged to be overexposed when the sky area loses its color or when flesh tones appear to be washed out. It may be said to be underexposed when the area of greatest interest to the observer is darker than preferred. These criteria are often related to the photometry of the scene only through statistics.

Effect of Viewing Conditions

The observer's judgment of preferred exposure is influenced to some extent by the projection system and viewing conditions. Some of the more obvious factors are:

a. A warm-colored light source often increases the observer's tolerance of slightly overexposed pictures.
b. The optimum exposure is not always the same for transparencies judged on an illuminator as compared to those projected on a screen.
c. Higher projection-screen brightness frequently leads to preference for slight underexposure because of higher color saturation.
d. Stray room light and surround brightness alter the apparent contrast and sometimes affect the exposure preference.

Suggested Conditions for Judging Preferred-Exposure Pictures

If a large number of pictures are to be judged for exposure preference, it is well to use definite and reproducible conditions for screening and viewing the films. Standardized procedures could include some of the following:

Type of screen	Matte
Color of screen	Clean, white
Screen brightness, no slide in holder	40 ± 5 ft-L
Color temperature of projected light beam—no slide	3000°K ± 50
Diameters enlargement of projected image	30 ×
Stray light at screen	0.05 ft-c max
Surround brightness	1 ft-L
Viewing distance	15 ft
Viewing angle from projector axis	±20°
Minimum eye-adaptation time	5 min
Minimum number of judges	3

Discrimination Accuracy

The difference, expressed in exposure value units, between the *actual exposure* and the *preferred-picture exposure* is the *discrimination accuracy* of a particular exposure-control design, but only for the one particular test scene.

The *discrimination accuracy* for at least twenty-five different scenes should be measured in determining the *discrimination accuracy* of a product.

The *discrimination accuracy* for at least one-hundred different scenes should be measured in evaluating the exposure constant K in Formula (1) as applied to a particular product.

Conclusion

Automatic exposure-controlled cameras can be precisely calibrated to give the *standard exposure*. On any one scene, the *preferred-picture exposure* is usually within 0.5 Ev of the *standard exposure* and results are quite satisfactory. However, on some scenes the difference may be as much as 1.0 Ev. The *preferred-picture exposure* cannot be exactly predetermined because it depends on artistic judgment and personal preference. However, automatic-exposure controls give more uniformly exposed films than most photographers are capable of producing by other means.

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Magnesium, A New Light Source in Flashlamps for Sequence and High-Speed Motion Pictures

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A short historical review describes artificial light sources, starting with magnesium in 1856 and leading to the zirconium-filled flashlamp introduced in 1957. The use of magnesium, aluminum, and zirconium follows logically from thermodynamic and kinetic considerations. The new use of magnesium for long-duration flashlamps in sequence and high-speed motion-picture photography is given in greater detail.

The application of a magnesium foil in the new long-duration "FloodFlash" lamp brings this old photographic light source back into practical use for sequence and high-speed motion-picture photography. A deeper understanding of the performance of the lamp will be gained by a short presentation of the history and the physical and chemical principles of flashlamps in general. A review of the technological development of flashlamps follows, and the differences in aluminum, zirconium, and magnesium flashlamps are pointed out. A more detailed description of the FF-33 FloodFlash lamp and practical data for its use are given in conclusion.

History of Combustible Metal Light Sources

A magnesium ribbon was used as an artificial light source for photography by Crookes as early as 1859.[1] Mixtures of magnesium powder with oxygen-yielding compounds and various applications in foil, wire, or powder form are described in patents dating back to 1866, with the latest patent issued in 1951.[2] The use of magnesium in aerial photographic bombs for military purposes will not be considered here.

Not until recently did magnesium foil find extensive use as a combustible in photographic flashlamps. Vierkoetter's patent in 1927[3] started the development of the glass flashlamp (Fig. 1A), and Ostermeier in 1929[4] disclosed an aluminum leaf-filled lamp (Fig. 1B) which incorporated most of the features of the modern flashlamp. The lamp consists of a closed glass envelope containing a metal in an easily ignitable form. The envelope is filled with oxygen gas. Two lead wires sealed into the glass carry the electric current from the base to a fine tungsten filament connected to them. The filament is heated rapidly, setting off two ignition beads glued to the ends of the lead wires. The burning particles from the exploding ignition paste start the combustion of the metal.

The improvements in the design of the photographic flashlamp since 1930 are considerable. The light output and the timing of the light output of flashlamps conform to Federal specifications.[5] The technology of producing uniform size and distribution of the combustible and the application of the ignition beads to a high degree of accuracy and reliability made the flashlamp a very popular device

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1. G. D. Rieck and L. H. Verbeek, *Artificial Light and Photography*, Elsevier Press, Inc., New York, 1952, p. 137, "Crookes, Use of Magnesium, 1859."
2. U. S. Patents 54,266 (1866); 407,351 (1889); 613,021 (1898); 2,201,294 (1940); 2,519,252 (1950); 2,571,799 (1951).
3. Paul Vierkotter, U.S. Patent 1,625,108 (1927).
4. J. Ostermeier, U.S. Patent 1,776,637 (1929).
5. *Supplement to Federal Specification for Lamps; Photographic, Flash, W-L-122-1958.*
   Federal Standard Stock Catalog, Sec. IV, Pt. 5.
   Federal Specification for Lamps; Photographic, Flash, W-L-122, 1945, or *Interim Revision W-L00122a (GSA-FSS), 1958.*

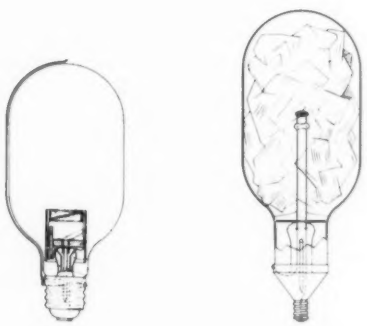

Fig. 1. First flash lamps with glass envelopes: (A) Vierkotter lamp, 1927, containing metal powder charge; (B) Ostermeier lamp, 1929, containing combustible aluminum foil.

TABLE I — Physical Constants of Metals and Metal Oxides Used as Combustibles in Flashlamps

Metal	Melting point, deg C	Boiling point, deg C	Std. heat of combust. at 25°C cal/mg O_2	Std. heat of combust. at 25°C cal/mg metal	Metal oxide at 25°C	Melting point, deg C	Boiling point, deg C	Color temp of lamp, deg K
Mg	651	1,107	8.99	5.92	MgO	2,800	3,300	3,800
Al	659.7	2,057	8.34	7.41	Al_2O_3	2,015	3,500	3,800
Zr	1,900	2,900	8.18	2.84	ZrO_2	2,700	4,300	3,950

in professional and amateur photography. The reduction in size of the lamp to miniature and subminiature types enhanced the relative simplicity of handling lamps and equipment. Last, but not least, a reduction in cost of picture taking was achieved through these developments. The flashlamp industry supplies at present over 600-million lamps per year[6] to the photographic market.

Chemical and Physical Principles of Flashlamp Technology

A short discussion of the scientific principles applied in the development of flashlamps may be helpful in understanding the flashlamp technology.

Thermodynamic Considerations

The combustion of the metal in oxygen gas produces the necessary calories to bring the combustion products up to the "maximum flame" temperature. The calculation of the maximum temperature has to take into consideration that the calories supplied by the combustion are not only used for heating, but also for melting, vaporization, and dissociation of the reactants and the combustion products. The existence of an ideal adiabatic process is also assumed. The hot gases and liquid droplets which form at high temperature are the light emitters in the lamp, as shown in Fig. 2. The radiated total energy is proportional to the fourth power of the corresponding temperature which the products have at any particular time, and the energy in the visible range of the radiation can be found by Planck's law. Thermodynamic calculations will therefore give only a theoretical energy distribution from which the color temperature can be estimated. The efficiency of a flashlamp can further be expressed in lumens per watt, whereby the measured visible light output is expressed in lumens, and the watts are found by converting the heat of combustion in calories at 25°C into wattseconds, assuming stoichiometric amounts of O_2 for the completion of the reaction present.

The heats of combustion for magnesium, aluminum, and zirconium per milligram of oxygen and per milligram of metal are given in Table I, Columns 4 and 5. The high efficiency of over 30 lm/w (Table II, Column 6) of zirconium, for example, cannot be predicted from the heat of combustion at 25°C. Consideration has to be given to the dissociation of the products also. One can conclude from the high boiling point—4300°C—of ZrO_2 that most of the energy of combustion will be used for reaching a higher temperature than when aluminum reacts with oxygen. Al_2O_3 dissociates at its boiling point of 3500°C,[7] which limits the color temperature to 3800°K. The color temperature of the zirconium-filled shred lamp is found to be 150° higher than that of the aluminum-filled lamp, as expected.

Kinetic Considerations

The ideal adiabatic condition cannot be achieved, but can only be approached by a relatively fast reaction to minimize heat losses. The reaction rate between the solid metal and oxygen gas is greatly

6. *Facts for Industry*, U.S. Department of Commerce, Series M36.

7. L. Brewer and A. Searcy, *J. Am. Chem. Soc.*, **73:** 5, 308 (1951).

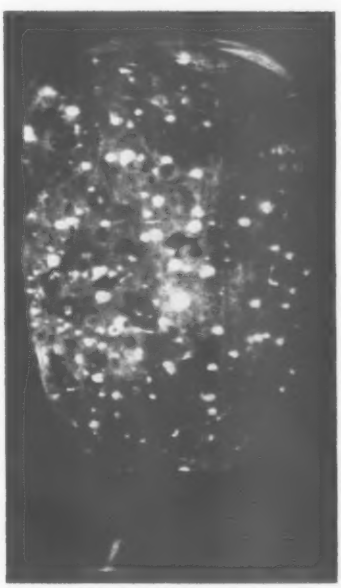

Fig. 2. High-speed motion picture of flashing zirconium lamp; M-25 lamp 40 msec after start of flash. White globules are either glowing liquid or solid ZrO_2.

TABLE II — Flashlamp Efficiency in Lumens per Watt and Lumen-Seconds per Milliliters of Lamp Volume

Lamp type	Metal fill	Lamp volume, ml	Total light output, lm-sec	Lm-sec/ml lamp volume	Lumens/watt	Year of introduction
#3	Al	232	110,000	475	19.5	1938
#25, #5	Al	30	20,000	660	19.2	1939
M-2	Al	7.3	8,000	1,100	17.2	1956
SF, SM	Zr	30	3,300	110	7.3	1940
M-25	Zr	7.3	16,000	2,200	33.6	1957
AG-1	Zr	1.2	8,000	6,700	29.8	1958
FF-33	Mg	232	150,000	650	16.8	1958

determined by the physical dimensions of the metal shreds. The greater the ratio of surface to mass, the faster will be the combustion. However, the transient pressure peak, which is determined by the initial fill pressure and reaction rate, must not be greater than the bursting strength of the lamp's glass envelope and its protective exterior lacquer coating. The aluminum-shred lamp does not lend itself to miniaturization because the peak pressure of the aluminum combustion is too high for the necessary initial pressure of several atmospheres. The zirconium-shred lamp, however, can be even subminiaturized without losing its light efficiency and still flash at a tolerable peak pressure. The magnesium foil acts quite differently from aluminum and zirconium. Fine magnesium shreds of the order of 1 or 2×10^{-6} sq in. at greater than atmospheric O_2 pressure will burn at half the light efficiency of a 0.005-in. thick foil. The magnesium foil in the FF-33 lamp burns for 2 sec, while aluminum foil 0.0005 in. thick will not ignite, and zirconium foil 0.0008 in. thick will burn only with a dim visible light emission. The vaporization of magnesium, a necessary step in the combustion,[8] occurs at 1107°C at atmospheric pressure, which is about 1000°C lower than for aluminum, and 2000°C lower than for zirconium. The heat losses at the vaporization temperature of magnesium are so favorable that the combustion can be maintained for 2 sec at high light efficiency.

Flashlamp Technology

A 0.00002-in.-thick aluminum leaf burned at low oxygen pressure was used in the first commercial flashlamps.[9] The timing and light output in such a lamp was poorly controlled by present-day standards. The aluminum leaf was then modified into a filamentary form, either by cutting shreds from thin foil or drawing an alloy of aluminum with 5–8% magnesium into fine wires. These lamps have an efficiency of 19 lm/w, as shown in Table II, Col. 6. The next step in lamp development, besides making smaller lamps, was the SF or SM lamp with fine zirconium metal powder as light-emitting combustible glued to the lead wires. This lamp with a light peak of 5 msec has an efficiency of 7.3 lm/w (Table II, Column 6). The change to above atmospheric oxygen pressure increased the lumens-seconds output per milliliters of lamp volume or the volume efficiency from 600 lm-sec/ml for a No. 25 lamp to 1,100 lm-sec/ml for an M-2 lamp, as shown in Table II, Col. 5. The introduction of zirconium shreds as combustible in the M-25 flashlamps doubled the lumens/watt efficiency compared to that of the aluminum-filled M-2 (Table II, Col. 6).[9] A further increase in volume efficiency was accomplished by making the lamp volume 1.2 ml with a corresponding increase in oxygen pressure, arriving at 6,700 lm-sec/ml (Table II, Col. 5) for the AG-1 lamp, with only a small loss in lumens per watt. The degree of lamp miniaturization is illustrated in Fig. 3. The volume of a No. 3 lamp is about 230 ml; that of an AG-1 lamp is 1.2 ml. With the intro-

8. K. P. Coffin, "Burning Time of Magnesium Ribbons in Various Atmospheres," *National Advisory Committee for Aeronautics Technical Note 3332*, Dec. 1954.

9. L. F. Anderson, *Illum. Eng.*, **53:** 657 (1958).

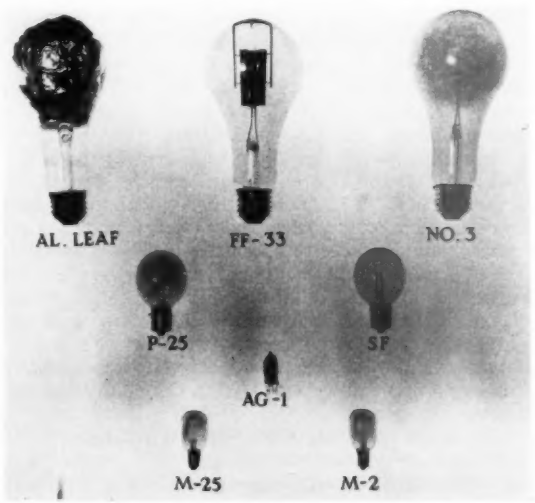

Fig. 3. Progress of miniaturization for photographic flashlamps. The lamp volume decreases from 230 ml (No. 3 lamp, aluminum filled) to 1.2 ml (AG-1 lamp, zirconium filled).

TABLE III — Guide NumberTable for Use of FF-33 FloodFlash Lamps in Connection with Sequence or Panoramic-Type Cameras

Exposure time, seconds	ASA Exposure Index									
	10–15	15–20	25–50	50–100	100–150	150–200	200	400	800	1600
1/2	88.4	104.5	153.1	216.5	279.5	330.7	353.6	500	707.1	1000
1/50	17.7	20.9	30.6	43.3	55.9	66.2	70.7	100	141.5	200
1/100	12.5	14.8	21.7	30.6	39.6	46.8	50	70.7	100	141.4
1/200	8.9	10.5	15.3	21.7	28.0	33.1	35.4	50	70.7	100
1/250	7.9	9.4	13.7	19.4	25.0	29.6	31.6	44.7	63.3	89.5
1/500	5.6	6.6	9.7	13.7	17.7	20.9	22.4	31.6	44.7	63.3
1/750	4.6	5.4	7.9	11.2	14.3	16.8	18.1	25.5	36.1	51.0
1/1000	3.9	4.7	6.8	9.7	12.5	14.8	15.8	22.4	31.6	44.7
1/1250	3.5	4.2	6.1	8.7	11.2	13.3	14.1	20	28.3	40

Note: To obtain lens aperture setting, divide guide number by lamp-to-subject distance in feet.

Following is an example of how a successful sequence camera scene was obtained:

Type Camera—Hulcher 70
Camera Speed—20 frames/sec
Shutter Speed—1/720 sec
Light Source—Two FF-33 lamps, one 5 ft and second 4 ft from subject. Open flash, both lamps simultaneously.
Type Reflector—Graflite 7-in.
Type Film—Ansco Super Hypan 70mm
Processing—15 min in DK60a, in constantly moving aerial film tank.

duction of magnesium foil used in the FF-33 long-duration lamp, one of the first metals originally used in artificial lighting appeared as a commercial product in a closed envelope. The lamp volume efficiency of 650 lm-sec/ml, the energy efficiency of 16.8 lm/w, make the lamp comparable to the aluminum-filled No. 3 or No. 25 lamp (Table II, Columns 5 and 6).

The FF-33 FloodFlash Lamp*

The use of the FF-33 lamp for sequence and high-speed motion photography is based on a usable light duration of 1.75 sec at an average light level of 60,000 lm, reached in 50 msec after starting the lamp. (See Ref. 10 for the light-time diagram and data for use in high-speed motion photography.) The color temperature is 3800° K, which is similar to a clear aluminum flashlamp, and has to be corrected with an 81-D Wratten filter for tungsten-light color film. The lamp can be flashed like an ordinary flashlamp with 4.5 v from three D-cells, and has the same size as a No. 3 flashlamp. An illumination level of 200,000 ft-c at a distance of 12 in. can be achieved in a 7-in. polished reflector, which is usually sufficient in high-speed exposures. Two lamps have also been used simultaneously at a distance of 4–5 ft from the subject to expose 28 pictures with a sequence camera. The *f*-stop settings for various exposure times for sequence or panoramic cameras are given in Table III, eliminating the need of special light meters.

The usable duration of 1.75 sec is not sufficient for the exposure of 50 or more feet of film for a "high-speed" motion-picture study if camera speeds of less than 900 ft/sec are used. Figure 4 shows the oscilloscopic trace of the light–time relation if three FF-33 lamps are flashed in sequence. The dip in light intensity is caused by the decreasing intensity of the preceding lamp and the increasing intensity of the following lamp. The dip is within the range of the average intensity level and can hardly be noticed when the film is projected at 16 ft/sec. A sequence timer can be easily assembled from commercially available parts. An example of such a timer is shown in the schematic wiring diagram, Fig. 5. The timing is accomplished by four Trans-O-Netic Time Delay Relays No. TJ-477-XAX, manufactured by the Heineman Electric Co., Trenton, N.J.[11] The delay relays are rated to

* FF-33 descriptive literature can be obtained from Sylvania Photo Sales, 1740 Broadway, New York 19, N.Y.

10. W. C. Fink, *Jour. SMPTE*, **68**: 599 (1959).

11. L. Szmauz and H. Bakes, *Electronics*, Sept. 25, 1959, p. 74.

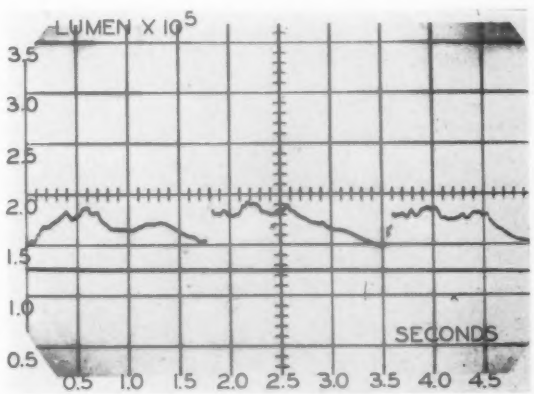

Fig. 4. Light–time characteristics of three FF-33 lamps flashed in sequence of 1.75 sec.

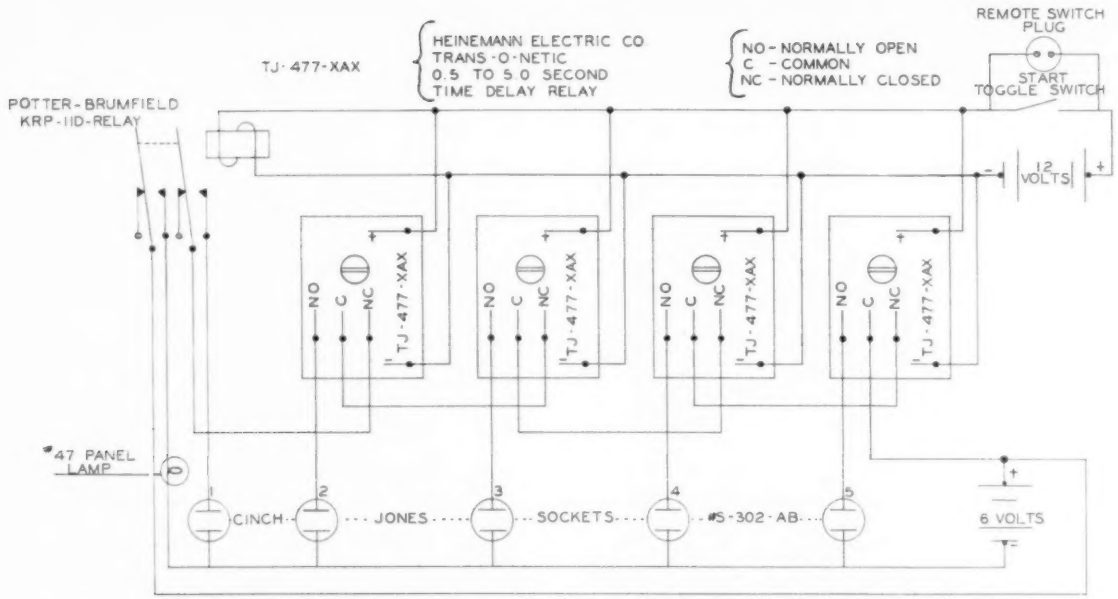

Fig. 5. Diagram of portable self-contained sequence timer for flashing FF-33 lamps when used at lower than 900-ft/sec camera speeds.

operate between 0.5 and 5 sec; however, the delay interval extends to 9 sec without any change in the electrical components. The closing of the toggle switch energizes the Potter-Brumfield KRP-11-D-Relay which closes the flashing circuit for the first FF-33 lamp and also starts the time delay relays. The first relay flashes the No. 2 lamp after 1.75 sec, the second relay flashes the No. 3 lamp 3.5 sec after actuating the toggle switch, and so on until all five lamps are flashed, giving a total light duration of 8.75 sec. The length of the intervals can be easily changed by resetting the potentiometers of the Trans-O-Netic Time Delay Relay. The time intervals can be calibrated with a laboratory timer, by replacing the FF-33 with 4.5 to 6-v incandescent lamps and observing the time when the lamps start to light up. The timer weighs only 10 lb and is being operated by twelve D-cells.

The time saving and simplicity in using such a self-contained light source together with the guide number table should make the FF-33 lamp a useful tool for professional high-speed motion picture or sequence photography.

Acknowledgment

The author wants to thank R. G. Petts, Head of the Electronic Section of the Photoflash Division of Sylvania Lighting Products, Montoursville, Pa., whose members participated in the development and building of the sequence timer.

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The 20× Precision Enlarger

R. D. PICKERING, *Apparatus and Optical Division, Eastman Kodak Company, Rochester, N.Y.*

A fixed magnification enlarger has been developed to produce 9 by 9-in. prints from small sections of a 70mm silver image negative (in a roll) with minimum loss of information. The instrument uses Koehler illumination and liquid immersion of the negative. The objective lens is a special design utilizing a narrow spectral response band and other compromises to achieve high definition. The instrument achieves 400 lines/mm in the central portion of the field and no lower than 200 lines/mm inside a 9-in. diameter circle on the print.

An enlarger has been designed to produce 9 by 9-in. prints at 20:1 magnification from small sections of a 70mm silver image negative in a roll of similar negatives up to 500 ft long. The major design aim was to make the quality of the system high enough so that there would be no loss of information from the original negative to the print. The negatives are to be made on moderate and fine-grain panchromatic aerial films with high-quality taking lenses. In terms of resolving power, the negatives will have about 100 lines/mm, more or less, depending on a variety of conditions. In order that no information should be lost in printing, the enlarger should be capable of about four times this or 400 lines/mm resolving power.

The Optical System

The illumination system is the Koehler type, following common practice in photomicrography to provide maximum sharpness. Referring to Fig. 1, the image of an iris diaphragm is formed at the fixed aperture stop of the objective lens by the condenser lens. The four parallel vertical filament coils of the lamp are imaged on the iris diaphragm by the relay lens. Magnifications and diaphragm diameter are designed so that the image of the width of the four lamp coils and the image of the wide-open iris just fills the fixed $f/2.0$ aperture stop of the objective lens. The calibration of the iris diaphragm scale is in terms of the relative aperture of the objective lens. A square mask in the midst of the relay lens is imaged on the negative by the field lens. The image of the mask is only slightly larger than the area of the negative being printed. This arrangement eliminates unnecessary light at the negative and the objective lens, reducing the problems of flare.

The objective lens was designed with a number of compromises which have permitted high performance levels in the restricted framework of this application. The six-element Planar-type design was chosen because of its capability for high relative aperture with a reasonable degree of field coverage. One disadvantage of the design is that its aberrations increase more rapidly than some other types as magnification departs from the nominal. The enlarger lens is adjusted for the 20:1 magnification specified with corrections added for a $^1/_8$-in.-thick glass plate in the

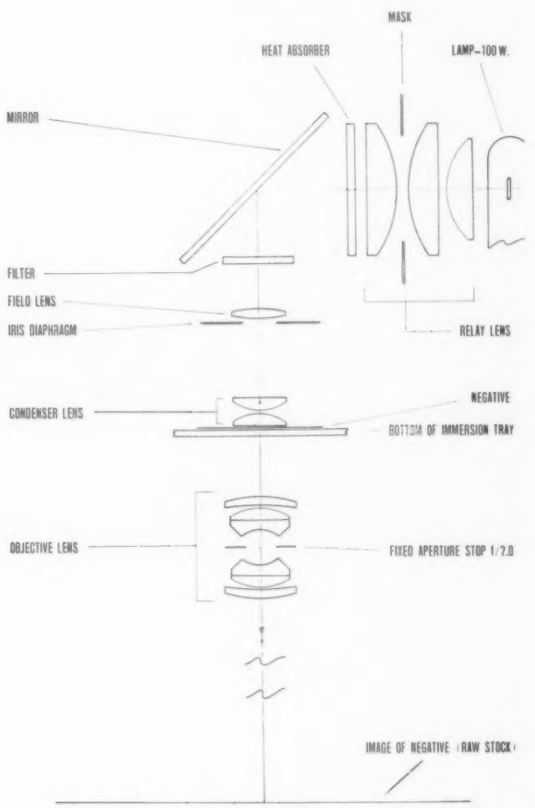

Fig. 1. Schematic diagram of the optical system of the 20× Precision Enlarger.

Presented at the Annual Conference, Santa Monica, California, 11 May 1960. Received 14 April 1960. The work described here was performed under Contract JP-635 with the United States Government. Patent application for the apparatus will be filed by the government.

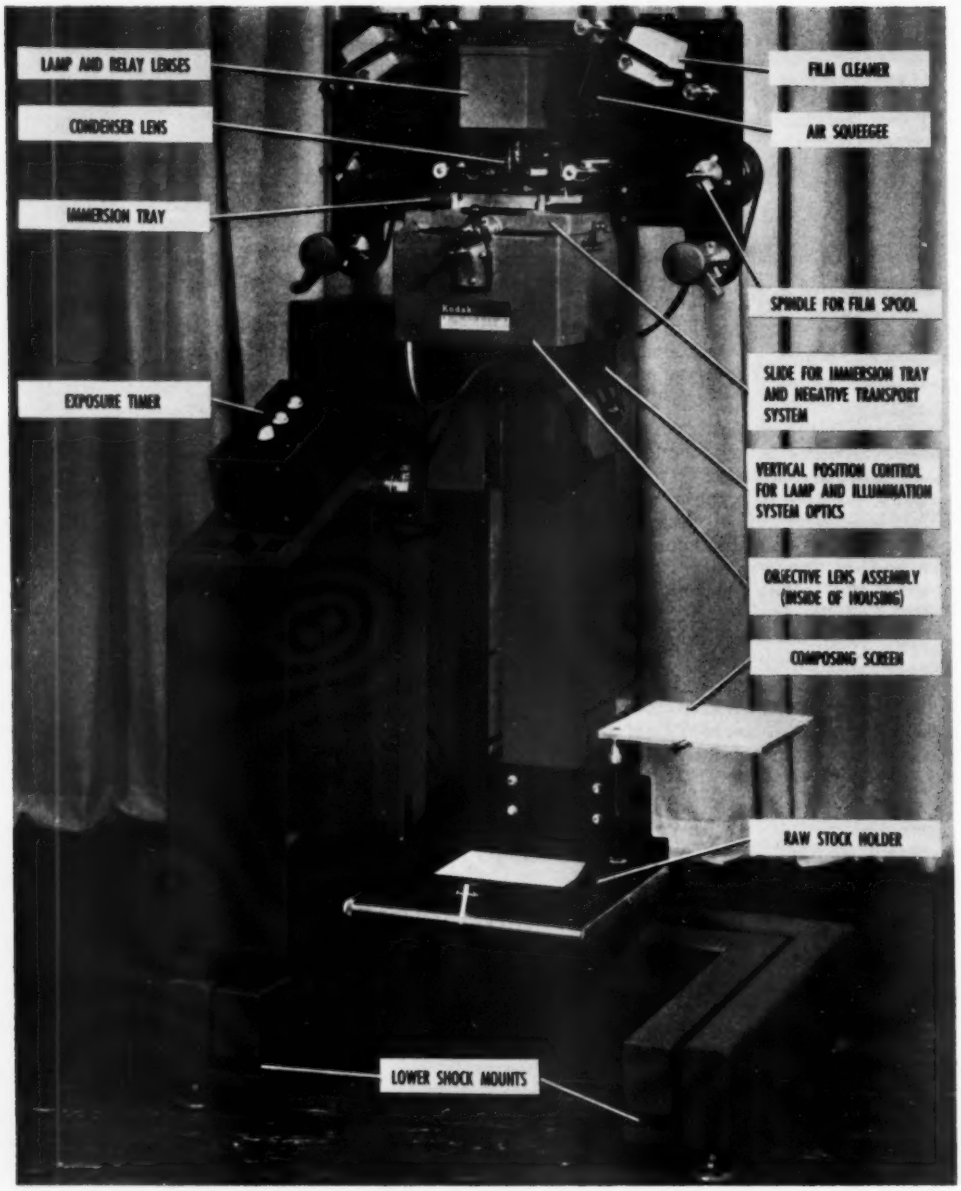

Fig. 2. General view of the 20× Precision Enlarger, with major visible subassemblies noted. Immersion liquid circulation and filtering system and ventilating hood not shown.

short conjugate. The field angle which the enlarger lens must cover is also relatively small. The majority of the print area, as enclosed in a circle tangent to the four sides of the square format, is within $6^1/_2$ deg of the lens axis.

The most productive compromise in terms of lens performance is in restricting the system to a narrow wavelength response band by the use of a color filter. This permitted the lens designers to use design parameters normally used in color corrections for the reduction of nonchromatic aberrations. Specifically, the lens is achromatized for 4050A and 4200A and is used for best performance with a second order Fabry-Perot interference filter with peak transmittance at 4200A and a band width of about 80A for transmittances over 50% of the peak transmittance.

The best resolving power in the central field is achieved with the iris diaphragm at $f/2.8$. Image quality at $6^1/_2$-deg field angle is best with the iris diaphragm at $f/4.0$. At smaller openings, the image is poorer over the entire field.

In order to obtain prints free of the scratch and

dust images for which any printing system with specular illumination is notorious, the negative is immersed in a liquid whose refractive index matches that of the film base. The negative in the printing position is clamped between the glass bottom of the immersion tray and the last surface of the condenser lens with light spring pressure. The immersion liquid used is a mixture of two organic compounds selected from a list of materials tested for this type of use by Delwiche, Clifford, and Weller.[1] The particular compounds chosen are 1,1,1-trichloroethane, whose refractive index is 1.438, and tetrachloroethylene, whose refractive index is 1.504. These two compounds are mixed as required to produce a liquid whose refractive index matches that of the film support or about 1.473 for acetate film.

No attempt has been made here to determine the permissible variation of refractive index of the liquid from that of the film base. Delwiche, Clifford, and Weller[1] report for their application that ± 0.02 appears to be a practical tolerance.

It should be noted that the refractive index of the liquid is matched to the film base and not to the gelatin of the emulsion. Deep scratches in the film base will disappear when filled with the index matching liquid. Light scratches on the emulsion side which are only in the gel overcoat will be obscured well enough without a perfect index match; but if there are scratches deep enough to disturb the image-bearing layer, replacement of the emulsion by a clear liquid, however perfectly matched in refractive index, would not restore the image. We must assume, when speaking of the ability to obscure scratches in the film, that no dirt is retained.

The two compounds selected for the immersion liquid are described as having:

1. Low effect upon the film—no short-term effect;
2. High volatility to promote quick drying of the film after immersion;
3. Nonflammability; and
4. Moderate toxicity, in which prolonged or repeated exposures or exposure to high concentration of the vapors may be harmful.

The low viscosity of the liquid permits the clamping of the negative between the glass surfaces to be a practically instantaneous operation. The low viscosity also permits removal of the liquid by air knife squeegees adapted from a design described by Ott and Lovick.[2] The immersion liquid wets but is not absorbed by the film; therefore, the film may be immediately rewound after the liquid is removed.

Mechanical Construction

Figure 2 is a general view of the enlarger. The machine stands 70 in. high, 36 in. wide and about 32 in. deep. The holder for the photosensitive printing stock (or raw stock) is the black assembly with the bright handle near the floor. In this unit, a metal plate with foam rubber support provides lateral locating guides and support for the raw stock. The emulsion surface of the raw stock is pressed against the underside of the black frame; thus supports of various thicknesses, such as paper, film, or glass plates, can be accommodated without shift of focus. The 20-diameters magnification of the optical system provides 20 squared or 400 times as great depth of focus at the raw stock as at the negative. For this reason, it has not been necessary to provide vacuum holding for the raw stock.

The white square just above the raw stock holder, the "Composing Screen," is shown out of position in Fig. 2, its normal position being as low as possible above the raw stock holder. While an exposure is being made, the screen is pivoted about its support rod 180 deg out of the projected beam, and then may be moved back into the beam for composition of a new picture.

The gray rectangular assembly with hand crank, labelled "Objective Lens Assembly" in Fig. 2, houses the objective lens and its focusing mechanism and serves as the fixed member of the slide which carries the negative holder tray and the film transport system.

By limiting the instrument to a single magnification, we receive several benefits:

1. It is not necessary to move the negative and lens assembly or the raw stock holder; hence, better mechanical alignment and rigidity can be obtained.
2. In a careful setup operation, the lens may be adjusted to the best focus position. At the order of performance we are seeking here, focus becomes a major problem.

Since it is necessary to move the objective lens only short distances for fine focusing at the single magnification, we have been able to use a flexure member support mechanism for the lens. This arrangement provides freedom from looseness and backlash in the lens positioning. The lens assembly is screwed into an intermediate sleeve to a coarse focus position and clamped firmly. The sleeve is supported by a concentric thin spring steel "washer" at each end. Flexure of the steel washers permits only the mode of movement required for focus adjustment in an amount necessary for fine focusing. The fine focus position is controlled by a lever linkage between a micrometer screw and the intermediate sleeve. The spring loading provided by the flexure members loads the lever linkage to remove backlash.

The negative transport mechanism, all on the vertical black plate at the top of Fig. 2, and the bright metal immersion tray are carried on the slide on top of the casting which houses the objective lens. With this arrangement, the film path remains straight for any position of the objective lens axis across the film web.

The film transport is driven by the hand cranks at the lower corners of the vertical black plate. The takeup and supply spools are directly above each

1. D. A. Delwiche, J. D. Clifford, and W. R. Weller, *Jour. SMPTE*, **67:** 678 (1958).

2. H. F. Ott and R. C. Lovick, *Jour. SMPTE*, **63:** 191 (1954).

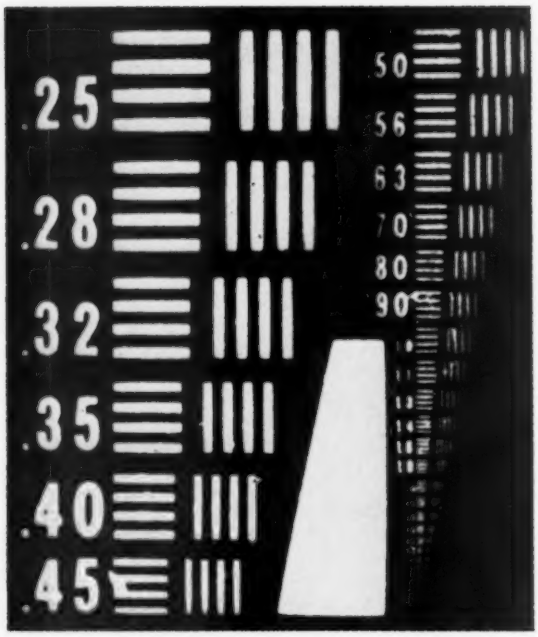

Fig. 3A. Enlarged section near the axis from a print made on the 20× Precision Enlarger. Original negative was made on Lippmann-type emulsion with a lens similar to the enlarger lens. Multiply numbers beside the resolution patterns by 200 to obtain the lines per millimeter on the negative. Compare this print with Fig. 4A.

crank. From the spools, the film passes over the first guide roll, through the corona discharge–soft brush cleaner unit, over the top guide roll straight down through the air squeegee, around the bottom guide roll and across, under the illumination system. The film transport system is open ended, so that a roll of negatives on two spools may be taken from an examination bench and, without rewinding it, the two spools may be loaded on the spindles and the film slipped into place over the guide rolls and into the air squeegees.

The lamp and illumination system optics are in the small grey box at the top center of the machine. The condenser optics and the iris diaphragm are in the bright metal cell extending downward between the two white guide rollers below the box. This assembly is mounted to move up and down through about 2 in., keeping the condenser lens axis in alignment with the objective lens axis. Control of the vertical position of the assembly is by the hand lever below and at the right of the slide support casting.

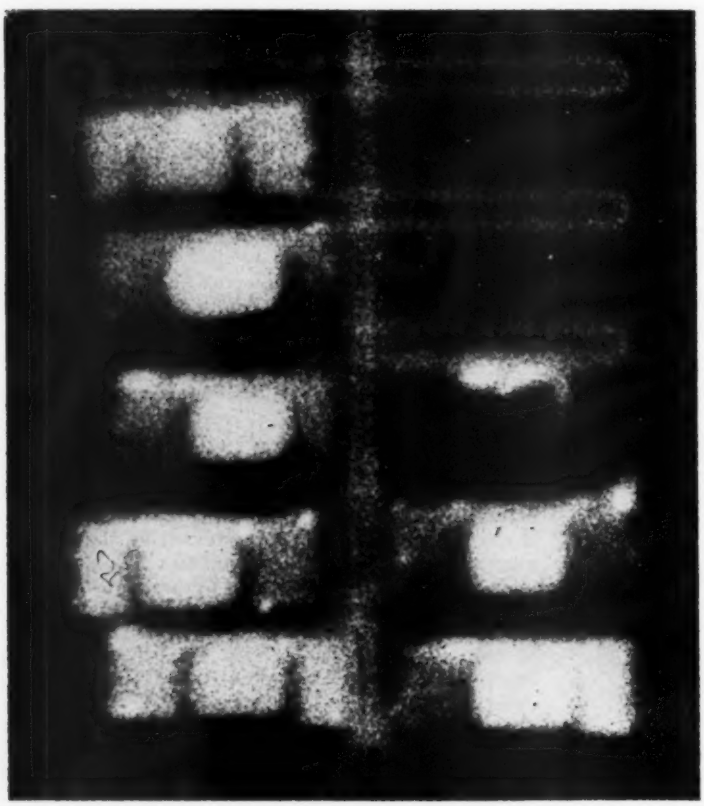

Fig. 3B. Enlarged section near the axis from a print of an aerial photograph negative made on the 20× Precision Enlarger. Original negative was made on fine-grain panchromatic film. The images of individual automobiles are less than 0.25mm on the original negative.

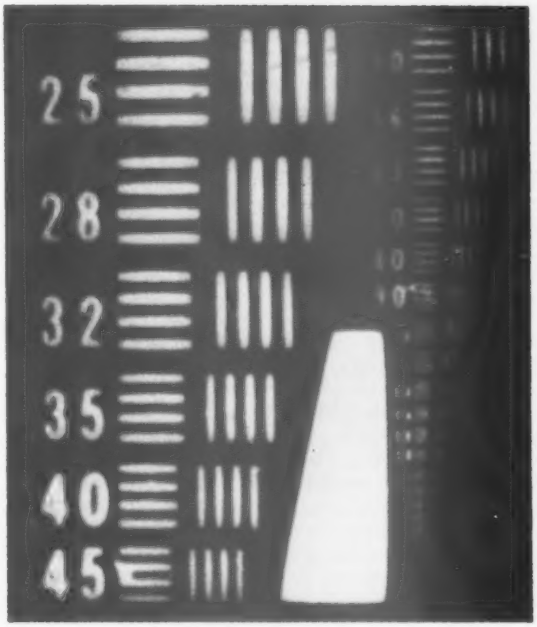

Fig. 4A. Enlarged section near the axis from a print of the same negative as was used in Fig. 3A, but made with a 2-in. Kodak Enlarging Ektar Lens on a popular condenser enlarger. Note lower resolving power in the fine patterns and less edge sharpness in the coarse patterns as compared to Fig. 3A.

Three detented positions are provided. The highest position is shown in Fig. 2 and is intended for loading, unloading, and rapid traverse of the film strip. In this position, the film is out of the immersion liquid. A second, intermediate, position lowers the condenser lens cell and the film strip into the liquid, leaving about 0.020 in. clearance between the condenser lens surface and the glass bottom of the tray. At this position, the image is in good enough focus to observe framing and yet the negative can still be moved about. The third and lowest position of the assembly clamps the negative between the condenser lens and the tray bottom, applies electric brakes on the film spindles and turns off the blowers on the film cleaner units. This position is used for exposure.

Continuous recirculation of about $1^1/_3$ gal of the immersion liquid is provided between two covered tanks through a filter, all at the left rear of the machine in Fig. 2. Flow from the upper tank of "clean" solution into the immersion tray is under gravity head of about 9 in. Overflow from the im-

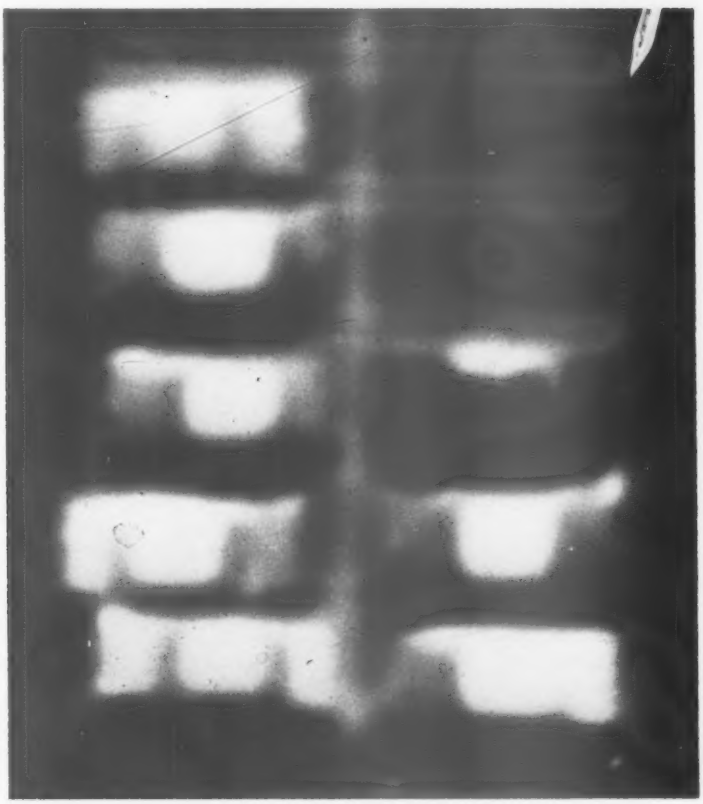

Fig. 4B. Enlarged section near the axis from a print of the same negative as was used in Fig. 3B, made with the same lens and enlarger as in Fig. 4A. Note the small difference in information obtained in the automobile images in Figs. 3B and 4B. Note also the negative grain structure imaged in Fig. 3B but not in Fig. 4B. This shows the high level of performance of the 20 × Precision Enlarger as compared to a high-quality negative and as compared to a good normal enlarger system.

mersion tray is through a flexible tube into the lower tank, also under gravity head. Solution stripped from the film by the air squeegees is discarded because of the possibility of moisture picked up from the film and from the air during removal from the film.

A rigid coupling is provided between the negative holder, the objective lens, and the raw stock holder by an aluminum box section beam with cross section of 4 by 8-in. outside measurement and about $^3/_4$-in. wall thickness. The entire optical system assembly is isolated from the outer frame of the machine by rubber shock mounts which provide a resonant frequency of about 15 cps. This frequency is much lower than any resonant frequencies in the optical system assembly. The shock mounts may be considered as mechanical filters to remove high frequencies which could excite resonances in the assembly.

Because of the moderate toxicity of the immersion liquid, a ventilation hood is provided to be mounted over the machine. This hood is equipped with an 8-in. axial flow blower which will be vented to the outdoors through 8-in. round pipe with a sufficient number of bends to accomplish light locking. A plastic curtain is suspended from the back and two sides of the hood to improve the efficiency of vapor removal.

Control of exposure in the enlarger is achieved by turning the printing lamp on and off. The exposures are timed automatically by a 3-decade laboratory timer which provides times to 111 sec in 0.1-sec increments.

Performance

A major problem in testing the performance of the enlarger has been to obtain negatives of resolution charts or picture matter of sufficiently high quality to produce prints limited only by the performance of the enlarger. We have made prints from negatives of somewhat less than this ideal quality, but they nonetheless indicate in a qualitative way the enlarger performance.

One negative is of a series of four-bar resolution charts photographed on a Lippmann-type emulsion at 20:1 reduction on a camera equipped with a form of objective lens similar to that on the enlarger. Our resolving power chart prints are thus second generation and do not present a true numerical statement of the resolving power capability of the enlarger, but in these second-generation prints, we have consistently achieved 400 lines/mm in the central portion of the field and no lower than 200 lines/mm inside a 9-in.-diameter circle on the print.

A second negative used is a 70 mm aerial photograph on fine-grain film, showing, in part, a shopping center parking lot. In this negative, the images of individual automobiles are less than 0.25mm long.

Figures 3A and 3B are reproduced from prints of these negatives, made on the 20X Precision Enlarger near the objective lens axis. For comparison, Figs. 4A and 4B are similarly reproduced from prints from the same negatives made with a 2-in. $f/4.5$ Kodak Enlarging Ektar lens on a popular condenser-type enlarger, using a No. 211 Photoenlarger Lamp, also near the objective lens axis. This system is representative of enlarging lens quality and illumination system used by many photographers to enlarge 35mm double-frame still pictures.

The numbers beside the groups of resolution charts should be multiplied by 200 to obtain lines per millimeter in the negative printed by the respective enlargers. In addition to the higher resolving power shown in Fig. 3A as compared to Fig. 4A, note the better sharpness of the edges of lines in the coarser resolution patterns.

We learn little more about the structure of the cars in Fig. 3B than in Fig. 4B only because the information is not available in the negative. The distinct images of the negative grain structure in Fig. 3B indicate the performance of the new enlarger is much better than that of the enlarger used to produce Fig. 4B. Also, it appears that the new enlarger's performance is much better than the camera lens and negative film system. These examples indicate success in our design goal of making the quality of our enlarger system high enough that there is no loss of information from a high-quality original negative to the print.

Acknowledgments

1. Mechanical design of the machine: O. Gnage and A. Lafontant under the supervision of R. E. Klauss.
2. Computation of the illumination system and consultant on the optical design: Dr. R. Kingslake.
3. Objective lens design: Dr. M. Hertzberger.
4. Consultants on photographic problems: R. Leavitt and G. Rudd.

All of the above are members of the technical staff of the Eastman Kodak Company.

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An Equation of State for the Photographic System

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The H&D curve, which relates density to exposure, is the most common characteristic curve for a silver halide photographic emulsion. The slope of the H&D curve and its position along the exposure axis varies with the degree of chemical sensitization or "digestion" or "after-ripening" received by the emulsion. Chemical sensitization, therefore, can be considered a third dimension to the H&D curve. This paper explores this three-dimensional or three-component system and describes some simple quantities, similar to the familiar "gamma," which relate all three variables.

Density (D), the degree of Exposure (E), and the degree of Chemical Sensitization (S) are related quantities such that any two determine the third. An equation of state for a given emulsion can be written: $D = f(E,S)$ of which the differential is $dD = (\partial D/\partial E)_S dE + (\partial D/\partial S)_E dS$. The familiar H&D curve is the special case $D = f(E,S_i)$, while the corresponding special case $D = f(S,E_i)$ is, in this paper, called the Sensitization Curve and is illustrated experimentally. From these expressions, it can be shown that $\gamma = \alpha\beta$, where γ is the familiar $(\partial D/\partial E)_S$, which is an abbreviated convenient form of the usual $dD/(d \log E)$, and α and β are $-(\partial S/\partial E)_D$ and $(\partial D/\partial S)_E$ respectively. Additional relationships are described.

This treatment of the photographic system does not depend on the mechanism or the chemical nature of the product of chemical sensitization or latent-image formation. Both E and S are considered as intensive quantities and independent variables, while D is an extensive quantity and a dependent variable. Similarities are noted between this concept of the photographic system and more common physical systems such as a stretched wire or a confined gas. This description of the photographic system is illustrated quantitatively for an experimental emulsion at both low and high exposure intensities. The quantitative nature of the system is characteristically different at the two intensity extremes.

Photographic scientists and engineers are concerned with the optical density of an area of developed silver, whether emulsions are being made or used. Photographic density is the result of a sequence of events beginning with manufacture and continuing through exposure and processing. Interrelations between these steps have long been recognized, especially between exposure and density.[1] The latter, particularly the H&D curve, are used most often to characterize sensitivity and contrast.

The slope of the H&D curve and its position along the exposure axis for a given emulsion varies with the degree of chemical sensitization or "digestion" or "after-ripening" received by the emulsion during manufacturing operations. The degree of chemical sensitization of commercial emulsions is factory controlled, and many photographic scientists and engineers rarely have the opportunity to observe the effect of this important factor. The emulsion chemist, however, is constantly aware of the wide range of sensitization under his control and, indeed, he usually considers sensitization rather than exposure or processing as the primary independent variable in his work.

Presented at the Annual Conference, Santa Monica, California, 13 May 1960. Received 12 April 1960.

1. C. E. K. Mees, *Theory of the Photographic Process*, Macmillan, rev. ed., 1954, Chap. 4.

Chemical sensitization, therefore, can be considered a third dimension to the H&D curve. This paper explores this three-dimensional or three-component system and describes some simple quantities, similar to the familiar "gamma," which relate all three variables.

The Sensitization Curve

Following the precipitation, ripening, and washing of a photographic emulsion, the characteristic curve (or H&D curve) assumes a relatively flat configuration, and the emulsion is relatively insensitive to

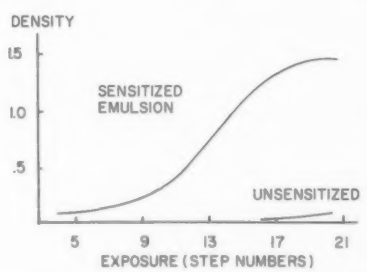

Fig. 1. H&D curves for an experimental emulsion (described in the text) at two extreme levels of sensitization.

light, compared with a sensitized ("finished" or "digested") version of the same emulsion grains. These extremes are illustrated in Fig. 1.

During the sensitization reaction ("digestion" or "after-ripening"), the H&D curve increases in slope (contrast) and sensitivity, as illustrated for a series of digestion times in Fig. 2. The examples shown are

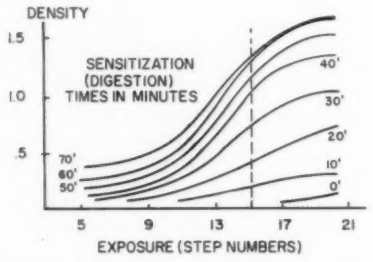

Fig. 2. A family of H&D curves (D vs E) for the same emulsion at several levels of sensitization, as indicated by sensitization time in minutes.

typical for a medium-grained bromoiodide (1.7% I) emulsion sensitized with a very "inert" bone gelatin containing a small quantity of sodium thiosulfate, of the order of 10^{-5} gram per gram of silver halide. These emulsions were sensitized or "digested" for varying periods of time under identical thermal and chemical conditions. Gold salts and sensitizing dyes were not employed. The emulsions were coated at a pH of 6.1, a pAg of 9.4, and a coating weight of 100 mg AgBr per square decimeter. Exposures were on a laboratory sensitometer. Exposure time was 0.08 sec, color temperature was 2700°K, and the log E value at Step 15 was -1.2.

For the purposes of this paper, development is constant. The type of developer will affect the quantitative nature of results, but will not alter any of the relationships to be derived. For both Fig. 1 and Fig. 2, and for the following illustrations, the emulsions were relatively completely developed for 5 min at 20°C in a Metol–hydroquinone developer of the following composition:

Metol	3.0 grams
Hydroquinone	9.0 grams
Sodium sulfite, anhydrous	50.0 grams
Potassium carbonate, anhydrous	50.0 grams
Potassium bromide	4.5 grams
Water to make 1 liter	

Each of the H&D curves illustrated in Figs. 1 and 2 is a plot of density (D) as a function of exposure (E) at some constant level of sensitization (S).

$$D = f(E, S_i) \qquad (1)$$

From a family of H&D curves for various levels of sensitization (digestion times), it should be equally possible to construct curves in which density (D) is a function of sensitization (S) at constant exposure (E).

$$D = f(S, E_i) \qquad (2)$$

Such a plot is illustrated in Fig. 3 using densities from the constant level of exposure illustrated in Fig. 2.

The reader will note that the degree or the extent of sensitization (S) has been indicated in units of time (minutes of digestion). This dimension is convenient and sufficient for this description and will be discussed in the next section of this paper.

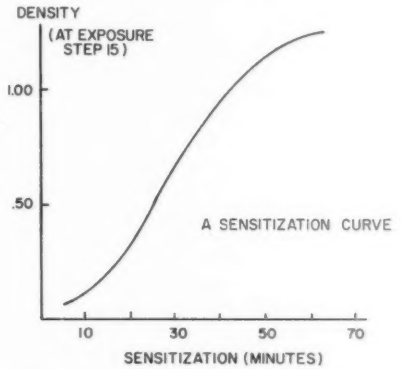

Fig. 3. Plot of D vs S, where D has been determined at Step 15 in the family of H&D curves shown in Fig. 2. The slope of this curve is $(\partial D/\partial S)_E$ or β.

The curve in Fig. 3 can be called a *sensitization curve* and is, like the H&D curve, only a single member of a family of such curves. It is apparent that both families of curves are a part of a more general and convenient description of this photographic system:

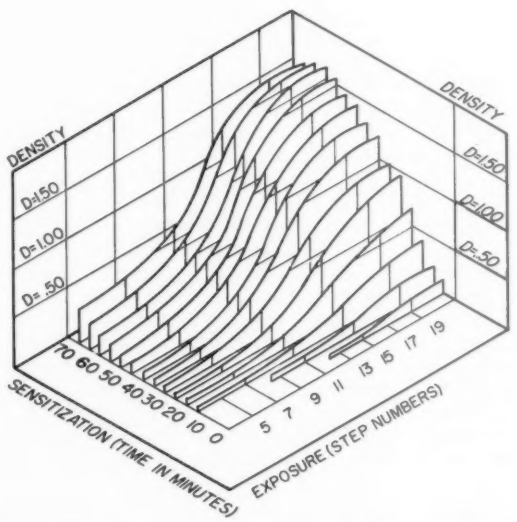

Fig. 4A. Three-dimensional drawing of the H&D curves for the emulsion described in the text, at a series of sensitization times. The surface of this model illustrates the equation, $D = f(E, S)$.

$$D = f(E, S) \quad (3)$$

This is an equation of state for the silver halide photographic system and expresses density in terms of the two most important independent variables, exposure and sensitization.

This more general description is illustrated, for the simple emulsion previously described, in the three-dimensional charts of Fig. 4. Two planes in the three-dimensional figure, at constant exposure and at constant density, are shown, for purposes that will be described below.

The "Dimensions" of Sensitization

Exposed grains in an emulsion are in a particular state or condition which makes them readily developable. Sensitized grains (grains which have been subjected to the chemical reactions of sensitization) also are in a particular state or condition which influences the effectiveness of the exposure. In this paper, the terms *exposure* and *sensitization* refer to these states or conditions and not to the mechanisms by which they were achieved. Similarly, the chemical nature of the latent image or the product of chemical sensitization is not a part of these considerations.

Exposure can be expressed very quantitatively in terms of time, intensity, wavelength, etc., but these specifications are *measures* of exposure and not the effect of exposure itself. Similarly, sensitization can be measured in terms of reaction time, temperature, and concentration of reactants such as thiosulfate, but time and the other variables are *measures* of sensitization and not sensitization itself.

If the remaining variables are constant, a single parameter is sufficient to measure either exposure or sensitization. For exposure, it is common to vary the intensity of light, but time-scale sensitometry is equally satisfactory for many purposes. For sensitization, a time scale is convenient, but temperature or concentration of reactants would be similarly usable. In this work, sensitization has been measured in terms of reaction time in minutes. Summarized in Table I are some of the more common experimental variables used to *measure* exposure and sensitization.

TABLE I — Common Measures of Exposure and Sensitization

Exposure	Sensitization
Time	Time
Intensity	Concentration
Wavelength	Temperature

Some Relationships and Definitions

Density (D), exposure (E), and sensitization (S) are three related quantities such that two determine the third. From Eq. (3), the equation of state, it follows therefore that:

$$dD = \left(\frac{\partial D}{\partial E}\right)_S dE + \left(\frac{\partial D}{\partial S}\right)_E dS \quad (4)$$

using the familiar classical technique of partial differential coefficients.[2] It appears that this function of E and S is continuous and, therefore, it also follows that:

2. E. A. Guggenheim, *Thermodynamics*, Interscience Publishers, New York, 1949, Chap. 3.

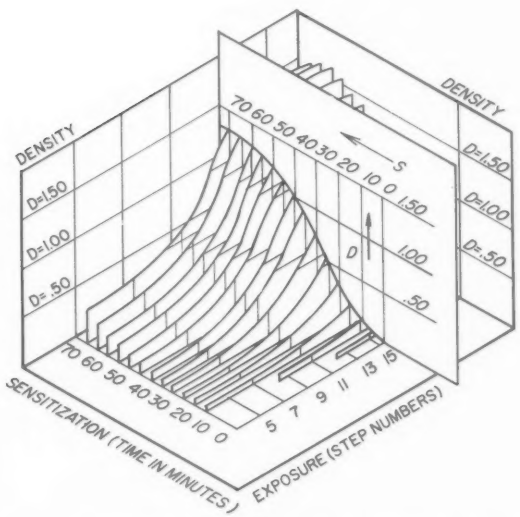

Fig. 4B. Drawing of a constant exposure plane intersecting the surface of the model shown in Fig. 4A. Line of intersection is the sensitization curve shown in Fig. 3.

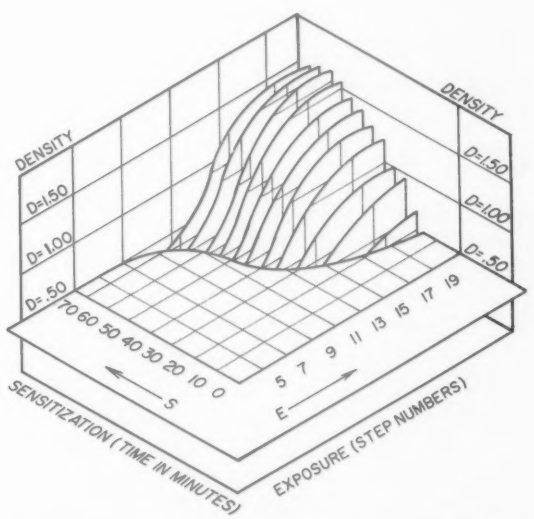

Fig. 4C. Drawing of a constant density plane intersecting the model shown in Fig. 4A. Line of intersection is the S vs E curve, several of which are illustrated in Fig. 5.

$$\left[\frac{\partial}{\partial S}\left(\frac{\partial D}{\partial E}\right)_S\right]_E = \left[\frac{\partial}{\partial E}\left(\frac{\partial D}{\partial S}\right)_E\right]_S \quad (5)$$

The latter "cross differentiation" identity is a consequence of the fact that, in two successive differentiations of D with respect to a continuous function of S and E, the order of differentiation is immaterial.

It also follows from the preceding relationships that:

$$\left(\frac{\partial D}{\partial E}\right)_S \left(\frac{\partial E}{\partial S}\right)_D \left(\frac{\partial S}{\partial D}\right)_E = -1 \quad (6)$$

The reader will recognize that, formally, the mathematics employed is the same as that normally used to derive many familiar relationships in thermodynamics.

The partial differential coefficients can be replaced with less cumbersome symbols by means of the following definitions:

$$\left(\frac{\partial D}{\partial E}\right)_S = \gamma \quad (7)$$

This familiar symbol for the slope or "contrast" of the H&D curve applies strictly only to $[\partial D/(\partial \log E)]_S$ or, in the usual notation which ignores sensitization, $dD/(d \log E)$. Also, the symbol γ usually applies strictly to the straight-line portion of the curve while in this case it is being applied to the entire curve—the latter generally symbolized by G. However, these conveniences for simplicity and a sense of familiarity introduce no important errors.

Next, we define:

$$\left(\frac{\partial D}{\partial S}\right)_E = \beta \quad (8)$$

Beta is the slope of the sensitization curve as described in the section on *The Sensitization Curve*, above; it is very similar to "gamma." The function β as used here is similar to the function R, the rate of sensitization, as used recently by W. D. Kelly,[3] except that in Kelly's paper R specifically represented $\log E = 1.45$.

Finally we define:

$$-\left(\frac{\partial S}{\partial E}\right)_D = \alpha \quad (9)$$

Alpha is the negative slope of the plot of S vs E at the same constant density, D, as illustrated in Figs. 4C and 5. This is the most interesting of the quantities derived and defined in this section since both S and E are the independent variables in this description of the photographic system.

The quantity $-\alpha$, in words, is a measure of the increase in degree of sensitization necessary to permit a unit decrease in exposure such that the same class of grains (constant density level) will remain developable. When $-\alpha$ is maximum the particular class of grains involved (D) have been sensitized to the point where the necessary exposure for developability is minimum. The value of E for maximum $-\alpha$ is, of course, a measure of photographic *speed* or *sensitivity* for the entire class of grains involved. This is the only way in which sensitivity, as distinct from sensitization, becomes involved in this discussion.

In terms of the simplified notation defined above, the equations developed in the beginning of this section become:

$$dD = \gamma dE + \beta dS \quad (10)$$

$$\frac{\partial \gamma}{\partial S} = \frac{\partial \beta}{\partial E} \quad (11)$$

$$\gamma\left(-\frac{1}{\alpha}\right)\frac{1}{\beta} = -1 \quad (12)$$

which rearranges to become:

$$\gamma = \alpha\beta \quad (12')$$

Experimental Illustration

The relationships outlined above can be illustrated experimentally. The emulsions used were described

3. W. D. Kelly, *J. Phot. Sci.*, **6**: 16 (1958).

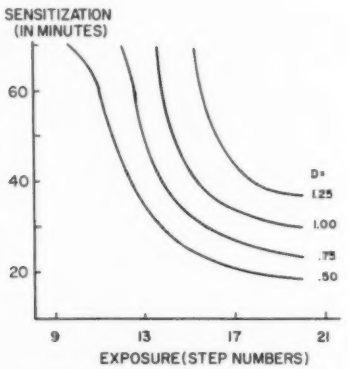

Fig. 5. Plot of S vs E at several density levels, for a high intensity exposure. These curves illustrate several of the planes depicted in Fig. 4C. The slope of these curves in $(\partial S/\partial E)_D$ or $-\alpha$.

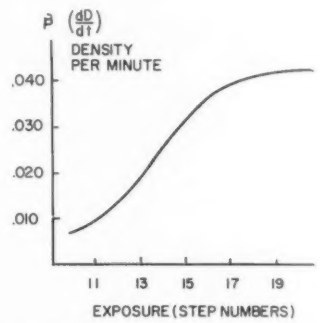

Fig. 6. Plot of β vs E. The values for β were obtained from a family of curves similar to Fig. 3 at sensitization equal to 40 min.

in the section on *The Sensitization Curve*, above, and illustrated in Figs. 4A, 4B, and 4C. H&D curves from this set of emulsions have been illustrated in Fig. 2 and a sensitization curve in Fig. 3. A plot of S vs E for several levels of D is illustrated in Fig. 5. A derived plot of β vs E is shown in Fig. 6. Another derived plot of γ vs S is shown in Fig. 7.

A check of Eq. (12′) can be made at any convenient location on the three-dimensional surface illustrated in Fig. 4. The point: $D = 0.50$, $E =$ Step 15 (for each step, $\Delta \log E = 0.15$) and $S = 40$ min will be used.

From Fig. 2, where the unit of E is $\log E = 1.0$:

$$\gamma = 1.2 \text{ (dimensions are } D, E^{-1}).$$

From Fig. 3, when the unit of S is time in minutes:

$$\beta = 0.02 \text{ (dimensions are } D, t^{-1}).$$

From Fig. 5, when the unit of E is $\log E = 1.0$ and the unit of S is time in minutes:

$$\alpha = +65 \text{ (dimensions are } t, E^{-1}).$$

Substituting these values in the equation $\gamma = \alpha\beta$ we see that

$$1.2 \cong (0.02)\ (65) \cong 1.3.$$

The agreement is reasonable, considering graphical data and the precision of laboratory emulsion experiments.

A similar check can be made of Eq. (11), i.e., the cross differentiating identity. In the same vicinity of the system from Figs. 6 and 7 and

$$\frac{\partial \gamma}{\partial S} = 0.025 \text{ (dimensions are } D, E^{-1}, t^{-1})$$

$$\frac{\partial B}{\partial E} = 0.022 \text{ (dimensions are } D, E^{-1}, t^{-1}).$$

These two quantities should be identical and, as in the previous case, the agreement appears to be satisfactory.

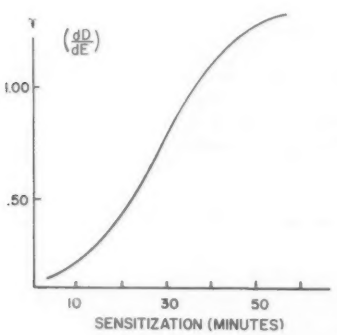

Fig. 7. Plot of γ vs S. The values of γ were obtained from H&D curves similar to those in Fig. 2 at exposure Step 15.

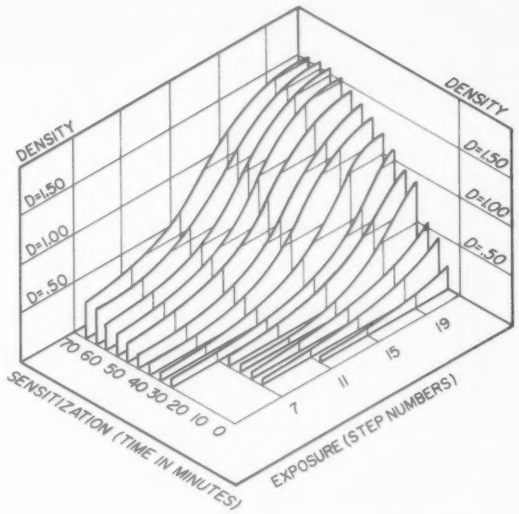

Fig. 8. Three-dimensional drawing of the H&D curves for the same set of emulsions illustrated in Fig. 4, but for a low intensity exposure.

Effect of Exposure Intensity

The relationships developed in this paper involve exposure, but do not explicity include exposure intensity. It is interesting, therefore, to examine the effect of exposure intensity on these relationships. The emulsion system previously described was examined with exposure intensities about 10^4 greater and 10^{-4} less than the exposure originally used. The high intensity exposure yielded a photographic system substantially similar to that described in the preceding section, but the low intensity exposures revealed interesting differences.

The three-dimensional model of the low intensity exposure system is illustrated in Fig. 8. It is evident that the system exhibits a relatively "flat" surface compared with the gently rounded configuration for

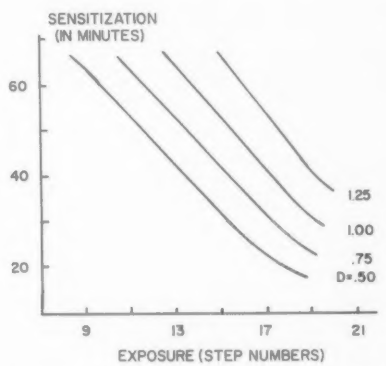

Fig. 9. Plot of S vs E at several density levels, similar to plot illustrated in Fig. 5 but for a low intensity level.

higher exposure intensities shown in Figs. 4A, 4B, and 4C. This is further illustrated by the almost linear S vs E curves in Fig. 9 compared with similar curves for higher exposure intensity in Figs. 4C and 5.

Numerical evaluation of D, E, S relationships similar to those in the preceding section is even more successful in the low intensity system, probably reflecting the more regular features of the plots and greater accuracy in obtaining graphical data. These additional calculations have not been detailed here.

Discussion

The nature of the changes in the D, E, S relationships with exposure intensity discussed in the previous section may relate to the latent-image mechanism. A discussion of latent-image mechanism is outside the scope of this paper, since the relationships are independent of the mechanism, but one feature is worthy of mention.

The slope of the S vs E curve, $(\partial S/\partial E)_D$, varies from very small to very large values for a given group of grains (density level) at high intensity exposures (Fig. 5). For low intensity exposures, the value of this function remains relatively constant for a wide range of both S and E (Fig. 9).

The quantity $(\partial S/\partial E)_D$ or $-\alpha$, in words, is a measure of the increase in degree of sensitization necessary to permit a unit decrease in exposure such that the same class of grains (constant density level) will remain developable. For high intensity exposures at high exposure levels, a relatively small increase in degree of sensitization will permit a large decrease in total exposure. Similarly, at high exposure intensity, with low exposure level, an increasingly large increment in degree of sensitization is necessary for relatively small decrements in total exposure. The particular class of grains (density level) appears to approach an exposure minimum limit in the high intensity system.

At low exposure intensities, however, the increase in degree of sensitization for a decrease in total exposure remains relatively constant over a wide exposure range for the system studied. The increase in sensitivity appears to have no limit other than the onset of emulsion fog[4] arising from excessive chemical sensitization. These differences at the extremes of the exposure intensity scale may be useful clues in the further understanding of reciprocity failure.

Other Variables of Interest

Other variables in the photographic process, such as development, also can be treated in this fashion. Development (degree of development or development time) can be added to the system described herein as a fourth variable or can be combined with density and exposure or density and sensitization for three-component treatment. Results are similar to those described in this paper and are not set forth in detail here.

Analogies with Other Physical Systems

This method of expressing the interdependence of exposure and sensitization invites comparison with more familiar physical systems such as a stretched wire or a confined gas.

Density may be considered a dependent variable, an extensive quantity, and a generalized displacement.[5] In these respects, photographic density is analogous to the volume of a gas or the length of a stretched wire. Exposure and the degree of sensitization can be considered independent variables and intensive quantities. The latter properties resemble the pressure and temperature of a gas as well as the tension and temperature of a stretched wire. These relationships are summarized in Table II.

TABLE II

System	Dependent extensive displacements	Independent intensive variables
Photographic	D	S, E
Confined gas	V	P, T
Stretched wire	L	t, T

Conclusion

The interdependence of sensitization and exposure in the photographic system has been recognized by workers in the field for many years. This paper offers a concise way of expressing the interdependence. The technique can be applied to other variables and to greater numbers of variables and may assist both in the practical use and theoretical interpretation of the photographic system.

Acknowledgments

The writer is indebted to Drs. D. R. White, T. D. Smith, and E. F. Haugh for their helpful criticisms during the preparation of this paper and to J. M. Pancza for the drawings.

4. R. W. Swenson, *Phot. Sci. & Eng.*, **1**: 119 (1958).

5. M. W. Zemansky, *Heat and Thermodynamics*, McGraw-Hill Book Co., New York, 1943, Chap. II.

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Volume 4, Number 4, July-August 1960

The Superadditivity of Mixtures of Hydroquinone and 3-Aminopyrazoline Derivatives

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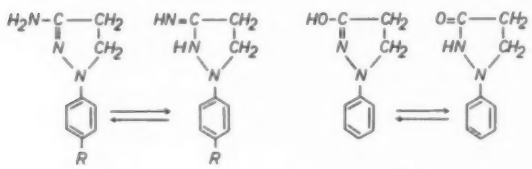
Para-amino derivatives of 1-phenyl-3-aminopyrazoline with hydroquinone show a developing action with pronounced superadditivity. Developer systems containing these derivatives have been studied and compared with systems containing 1-phenyl-3-pyrazolidone. It has been found that developers containing the 3-aminopyrazoline derivatives have a shorter induction period, and lower concentrations of the agent are required for maximum superadditivity. This is explained on the basis of the charges on the ionic species involved.

In spite of the structural relationship between 1-phenyl-3-aminopyrazoline (Compound I) and 1-phenyl-3-pyrazolidone (Phenidone*) (Compound II), the former does not possess any developer qualities of significance. Highly active developers or development accelerators can be obtained, however, by the introduction of an amino group into the para position of the phenyl nucleus[1] (Compound III). The methylated compound, Compound IV, acts in a quite similar manner as far as the kinetics of development are concerned. It is remarkable that a very pronounced superadditivity is obtained when the aminopyrazoline is present in addition to hydroquinone.



I, R = H
III, R = NH_2
IV, R = $NHCH_3$

II

Eggers[2] investigated the development kinetic behaviour of III in sulfite-free solutions as a function of pH and showed relations between activity and ionic species. Of interest to us were the conditions for maximum superadditivity of III and IV with hydroquinone in comparison with 1-phenyl-3-pyrazolidone (II), for which detailed investigations had been made by Axford and Kendall.[3]

Experimental Procedure

The investigated systems had the following composition:

Constant total concentration of the mixture of hydroquinone + III (IV or II)	10	mmole/liter
Na_2SO_3	50	mmole/liter
KBr	8.4	mmole/liter

The pH adjustment was carried out with NaOH buffered by a phosphate-borate-citrate mixture according to Teorell and Stenhagen,[4] which was also used by Eggers.[2] Two experimental series with pH values of 9.9 and 11.7 have been studied.

As photographic material, Agfa Phototechnical Film B (unsensitized) was employed. Narrow strips of 12 by 300 mm size were exposed behind a gray wedge with a logarithmic exposure increment of 0.30. Development was carried out within 24 hr after exposure. All developer solutions were maintained at 20°C. A 2% acetic acid solution served as a stop bath, while ordinary acid fixing solution was applied for fixing.

The simple arrangement shown in Fig. 1 was used to prevent subjective errors in the agitation of the material to be developed. With the emulsion side facing out, the exposed film strip was wound helically onto the cylinder and attached by means of a small rubber band. It was then inserted into a large test tube containing 50 ml developer solution in such a manner that during the rotation around the indicated axis no liquid was permitted to emerge. Two thirds of the test tube was filled by the de-

Presented at the Annual Conference, Santa Monica, California, 12 May 1960. Received 27 April 1960.

* Registered trade mark of Ilford Ltd.

1. German Patent 945,606 (U.S. Patent 2,852,374).
2. J. Eggers, *Wiss. Photogr., Ergebnisse der Intern. Konf. Köln*, 1956, p. 379.
3. A. J. Axford and J. D. Kendall, *J. Phot. Sci.*, **2**: 1 (1954).
4. T. Teorell and E. Stenhagen, *Biochem. Zeits.*, **299**: 417 (1939).

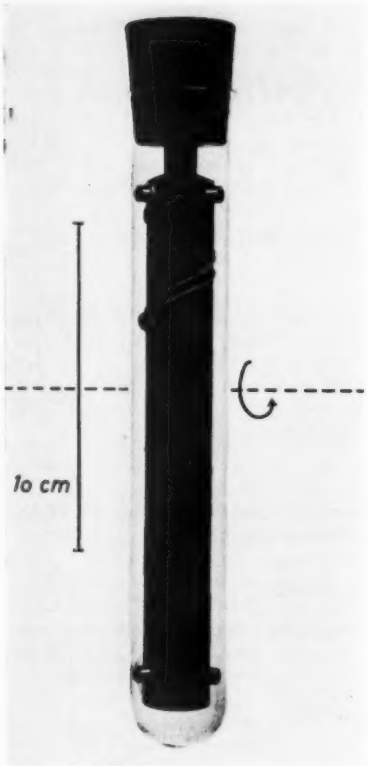


Fig. 1. A developing chamber.

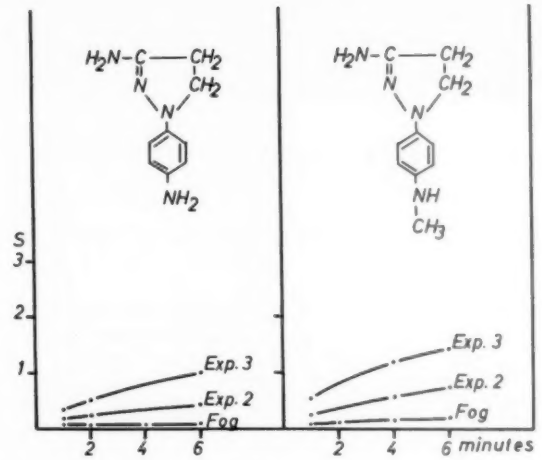


Fig. 2. Density (S)-time of development curves for Compounds III and IV. Developing agent—10 mmole/liter; sodium sulfite—50 mmole/liter; KBr—8.4 mmole/liter; pH 9.9. "Exp." refers to exposure level (see text).

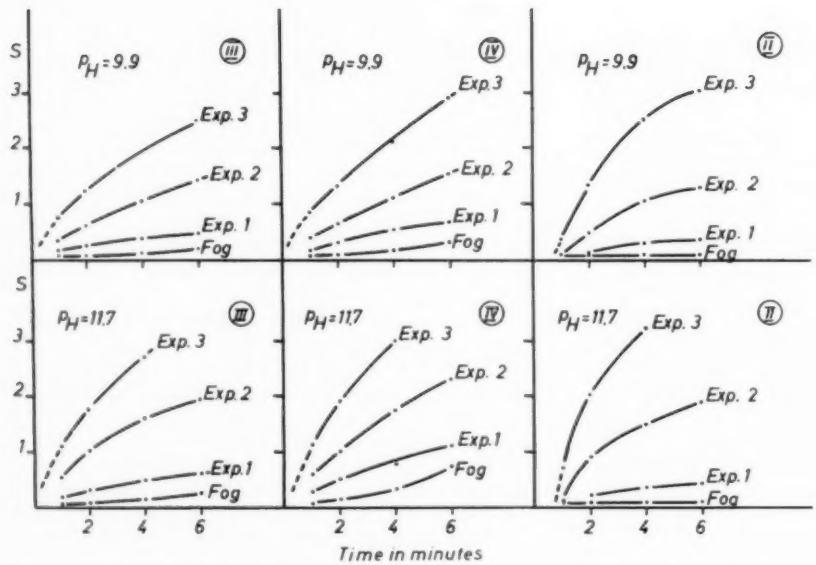


Fig. 3. Density (S)-time of development curves for mixtures of Compounds III, IV, or II (6 mole %) and hydroquinone (94 mole %) at pH 9.9 and pH 11.7.

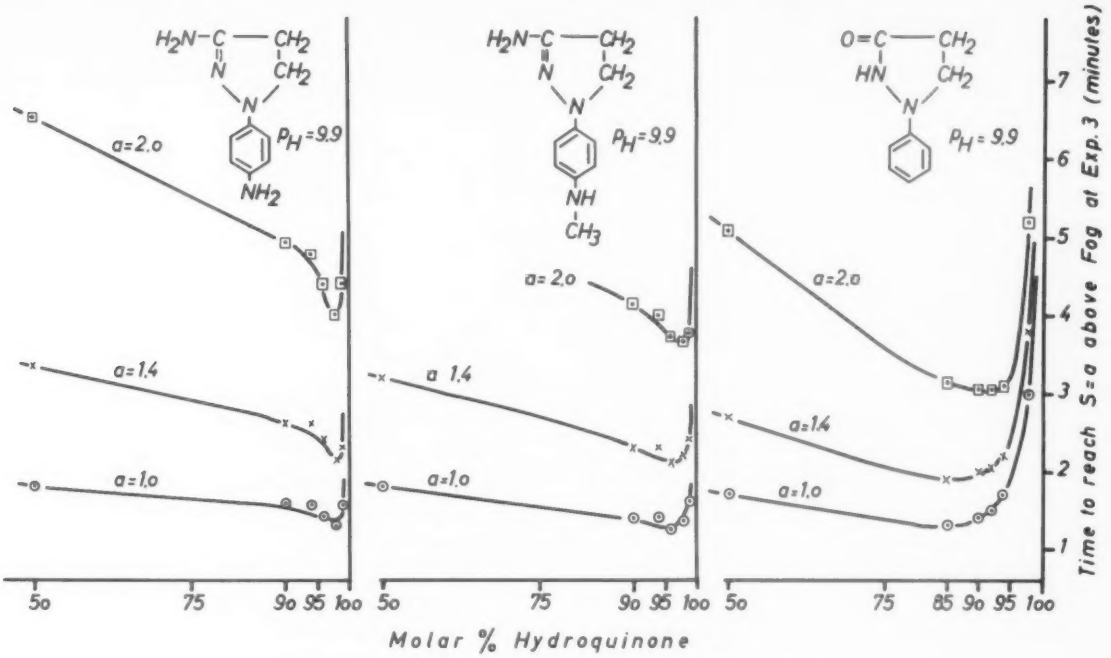

H_2N-C CH_2 N CH_2 N NH_2 P_H=9.9
H_2N-C CH_2 N CH_2 N NH CH_3 P_H=9.9
O=C CH_2 HN CH_2 N P_H = 9.9
a=2.0
a=1.4
a=1.0
a 1.4
50 75 90 95 100 50 75 90 95 100 50 75 85 90 95 100
Molar % Hydroquinone
Time to reach S=a above Fog at Exp. 3 (minutes)
1 2 3 4 5 6 7

Fig. 4. Superadditivity of Compounds III, IV, and II with hydroquinone at pH 9.9.

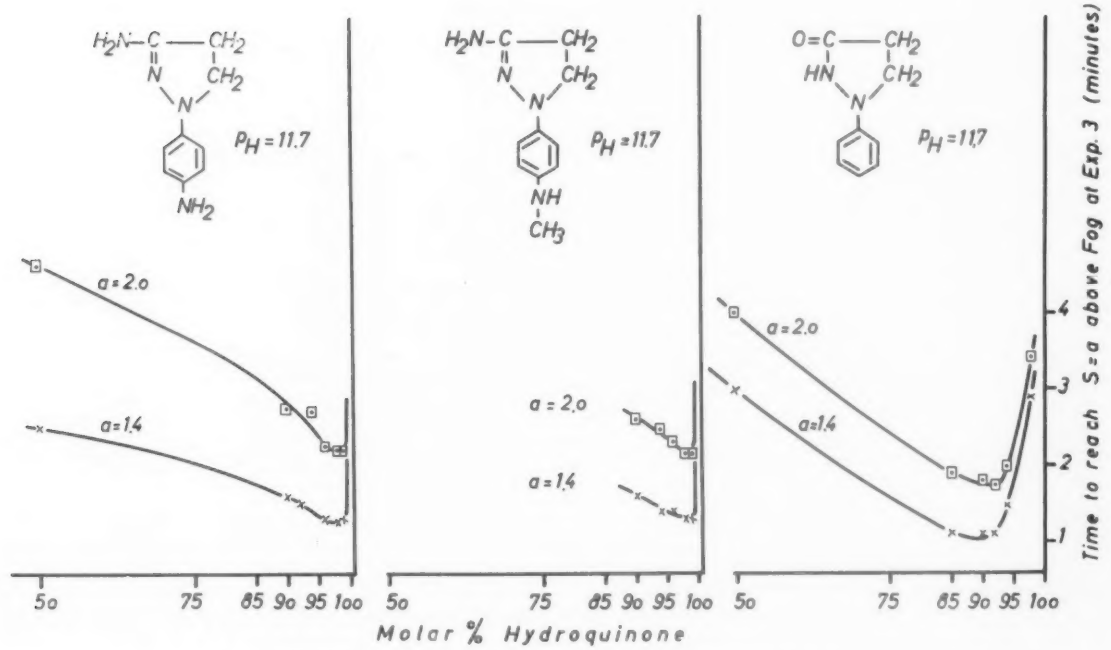

H_2N-C CH_2 N CH_2 N NH_2 P_H=11.7
H_2N-C CH_2 N CH_2 N NH CH_3 P_H=11.7
O=C CH_2 HN CH_2 N P_H=11.7
a=2.0
a=1.4
a = 2.0
a = 1.4
50 75 85 90 95 100 50 75 85 90 95 100 50 75 85 90 95 100
Molar % Hydroquinone
Time to reach S=a above Fog at Exp. 3 (minutes)
1 2 3 4

Fig. 5. Superadditivity of Compounds III, IV, and II with hydroquinone at pH 11.7.

veloper in such a way that all exposed parts of the film strip were below the surface of the liquid when the tube was held in a vertical position. Six of these tubes were placed side by side in corresponding bores of a block of plastic material. Subsequently, the whole unit was set in motion around the indicated axis at 30 rpm by means of an electric motor.

For each individual test, a fresh developer solution was prepared at least $^1/_2$ to 2 hr before use. By using the same time of development for each of the six test tubes simultaneously, we obtained five tests with the developing agents having different relative molar concentrations. The sixth test tube, containing a diluted Metol–hydroquinone developer, was used as a control.

After measuring the gray-scale steps obtained in this manner for three different exposures and the fog, the density development-time curves were plotted. Exposure 1 corresponds to a weak exposure close to the threshold; the two higher exposure levels, 2 and 3, have a log E difference of 1.0 and 2.5 respectively, compared to exposure 1.

Results

Figure 2 indicates that although III and IV by themselves initiate development immediately, their action is still relatively slow and flat. The growth of fog with IV is quite considerable. Apart from the fog, however, the development kinetic behavior of the aminopyrazolines reminds one of the behavior of 1-phenyl-3-pyrazolidone.

For the composition 94 mole % of hydroquinone and 6 mole % of III, IV, or II, results measured at the pH values 9.9 and 11.7 are given in Fig. 3. The point of convergence of the families of curves (dotted curve) corresponding to III and IV is located at smaller abscissa values than the one corresponding to II. This means that the induction periods of aminopyrazoline systems are smaller. These findings correspond with the visual impression of the appearance of the first image traces in the development of films or papers. They are not limited to the mixture proportion of 94 mole % of hydroquinone. The other compositions investigated indicate a similar behavior.

In Figs. 4 and 5, one of the possible methods of representation for the description of superadditivity was selected. The measuring points have been determined by graphic interpolation. Of course, when superadditivity is at the maximum, the curves show a minimum. It can be seen that III and IV are similar in their behavior. With the maximum superadditivity at 2–3 mole %, they clearly show maxima at lower concentrations than does II.

Discussion

The above mentioned results can be interpreted by the findings of James,[5] according to which the negative charge barrier around the silver halide grain has such an influence on the kinetics of development by anions that anions carrying several negative charges have a longer induction period than less highly charged ions or neutral molecules. In alkaline solution, II represents a simple negatively charged ion, while III and IV are neutral.

The aminopyrazolines easily form a blue radical,[2] whose existence in the meantime has also been shown by Eggers's measurement of the electron resonance.[6] This radical, being easily reduced by hydroquinone, probably plays an important part in conveying electrons to the grain surface.

The aminopyrazoline derivatives conform to the developing agent structure rule of Lumière-Andresen-Kendall, which was expanded by Pelz,[7]

$$X—(A{=}B)_n—Y \text{ is a developer,}$$

where X, Y = OH, NR_2;
R = H or a hydrocarbon radical;
A, B = C(R) or N; $n = 1, 2, 3 \ldots$

in a two-fold manner: first in the pyrazoline ring system, and, in addition, as a derivative of *p*-phenylenediamine. Thus, an intramolecular linkage of two effective configurations is evident.

5. T. H. James, *J. Franklin Inst.*, **240:** 15, 83 (1945).
6. J. Eggers, to be published.
7. W. Pelz, *Angew. Chem.*, **66:** 231 (1954).

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Tropical Storage of Processed Negatives

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I. A. OLIVARES, *Kodak Tropical Research Laboratory, Panama, R.P.*

Fungus growth on negatives may be prevented or greatly reduced by enclosure in an envelope impregnated with a suitable fungicide. Additional protection is offered by interleaving with treated paper when more than one negative is enclosed. The most successful of the fungicides tested was sodium pentachlorophenate. Envelopes made from paper impregnated with this fungicide protected negatives against fungus growth for periods up to eight years under moist tropical conditions. The use of nonaqueous adhesives, of edge seams, and of flaps closing the envelopes also contributed to stability. Specific recommendations for storage envelopes and interleaves are made.

Photographic negatives are readily attacked by fungi when stored under warm, humid conditions (above 65% RH). The fungi consume the gelatin and, while temporarily deterred by the silver image, they may soon attack the entire negative, which eventually becomes densely veined with fungus hyphae (Fig. 1). Early growth may be wiped off without leaving a pattern, but prolonged attack produces staining, etching, and actual degradation of the gelatin to the point where the image of the negative may be destroyed beyond recovery. The deterioration of negatives by fungus attack is more prevalent in the tropics where conditions of high temperature and humidity exist for protracted periods. However, serious fungus attack is known to occur under the moist storage conditions which can prevail during the summer in more temperate climates.

Communication No. 2069 from the Kodak Research Laboratories, presented at the National Conference, Chicago, 20 October 1959. Received 21 January 1960; revised 4 May 1960.

Several methods have been investigated in attempts to prevent fungus attack on negatives. Among these, treatment with chemical fungicides, coating with waterproof lacquers with or without appropriate fungicides, and the use of treated envelopes and interleaving paper have offered encouraging results. The scope of this paper has been limited to a summary of the work on negative storage envelopes and interleaves. The improvement in envelopes is important, since conventional storage envelopes offer only a very temporary protection to the negative, which is further reduced if the envelopes have open ends and thumb cutouts. Moisture-

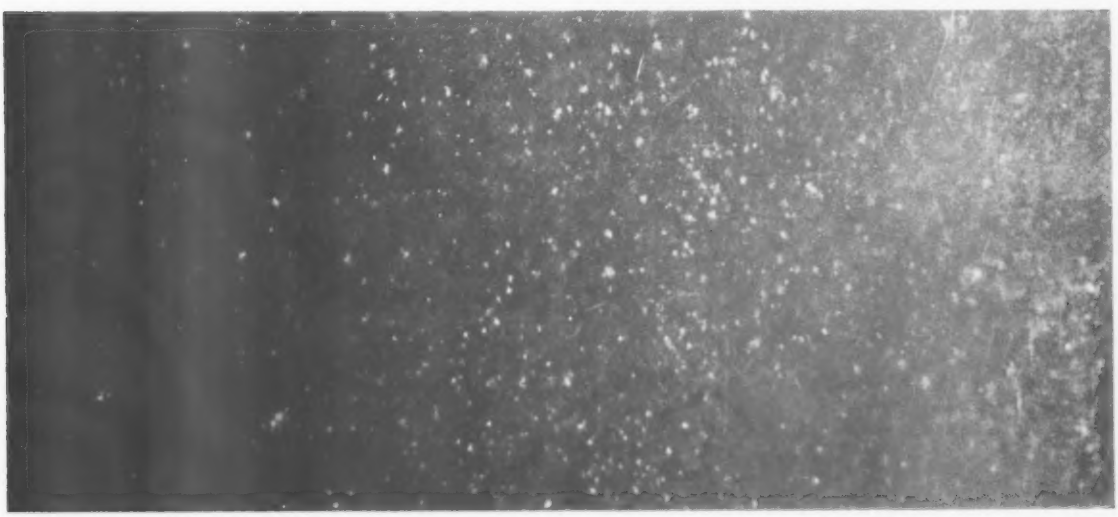

Fig. 1. Colonies of fungi growing on the surface of a negative which has been stored in the tropics.

Fig. 2. Test building for tropical deterioration studies, Barro Colorado Island, Panama Canal Zone.

absorption by the glue employed often causes local fading and accelerated fungus growth in the region of the seam, while the envelope and its adhesive may in themselves support fungus growth.

Description of a Typical Test

The experimental conditions and procedures employed in the tropical tests will be illustrated by examining one test in detail. Fourteen other tests were conducted to confirm the findings of the one described here and to examine other variables. The effect of these variables will be summarized in the next section.

This particular large-scale experiment involved the exposure of 112 negatives in 40 envelopes. The envelopes, prepared from a heavy duplex (laminated) photographic-grade paper, were bathed in solutions of the fungicides and dried between photographic-grade blotters. The fungicides selected were of widely differing types: zinc fluosilicate, a mixture of two quaternary fungicides, and the sodium salt of pentachlorophenol. All solutions were aqueous.

Processed negatives were stored under a series of varying storage conditions, using quadruplicate samples throughout. The test distribution may be outlined as follows:

a. Unprotected negatives (controls).
b. Single negative in untreated envelope.
c. Single negative in treated envelope
d. Four negatives in untreated envelope.
e. Four negatives in treated envelope.
f. Four negatives in untreated envelope with untreated interleaving sheets.
g. Four negatives in untreated envelope with treated interleaving sheets.

Samples from each of the categories in this test were hung from wires, while the bulk were stored on edge on shelves, with suitable separators between them.

Tropical Exposure Conditions

All field tests connected with this program were conducted at a field station in a clearing in the jungle of Barro Colorado Island in Gatun Lake, in the Canal Zone.

The Kodak Test Table consists of a well-ventilated building, erected about 7 ft above ground, on sturdy supporting pillars, protected from the tropical rains and direct sunlight by an overhanging roof, and adjacent to the jungle wall. Wooden shelves, stainless-steel wires, filing cabinets, etc., are employed to store photographic materials and equipment in a manner similar to that encountered in normal photographic practice throughout the tropics. Test materials in this building are subjected to full attack by moisture and fungi. There are no windows, but all open spaces in the walls are screened to avoid the entrance of large insects other than roaches, ants, silverfish, and mites (Fig. 2).

As is characteristic throughout most of the tropics, the climate of Barro Colorado Island shows the phenomenon of a distinct "wet" and "dry" season yearly. Data compiled from approximately 12 years' continuous recordings of the temperature and humidity inside the Test Table building indicate that maximum humidity approximates 100% daily, whereas the minimum varies from 63% to 75% in the wet season to about 50% to 60% during the dry season. Because of the surrounding tropical forest, the temperature in the building shows little variation throughout the year, the average temperature being 81° to 82°F.

The test samples were observed at intervals of four to eight months during the first two years' exposure, and yearly thereafter. Notations were made of the condition of each sample with respect to the degree of fungus attack, physical properties, fading, and the condition of envelope seams, etc. Serious deterioration of unprotected negatives was evident after one year and progressive deterioration was noted after this, although most of the changes during the balance of the $5^1/_2$ years' test period comprised intensification of deterioration observed prior to this time. The observations made during the test are in agreement with those made in the other tests. To avoid duplication, the results of all tests are summarized in the following section.

Summary of Results

A number of variables in envelope construction, fungicide composition, and storage conditions have been investigated. The importance of these factors is discussed, but no experimental details or observations are included.

The Materials Employed for Envelope Construction

(a) *Paper Envelopes.* Heavy, closely woven papers, including laminated duplex paper, were quite

satisfactory. Brown kraft papers of the type commonly used for wrapping were very effective, the tight weave holding the fungicide well. The 33- and 50-lb stocks were preferred over the 25-lb, which was a little light. Treated glassine papers were excellent and strongly inhibited fungus growth. Unsized paper did not fully restrain fungus growth even when impregnated with the most effective fungicides. Untreated manila tag envelopes of the sort commonly used for negative storage gave little protection to the negative and were themselves badly attacked.

A number of the envelopes were colored and the dyes tended to fade badly, giving a poor appearance. On the other hand, white envelopes soiled readily. The brown kraft paper envelopes were very light-stable and generally satisfactory.

Fungicide-impregnated papers were not available commercially at the time this work was begun, but during the course of these experiments such papers did become commercially available for wrapping fruit, soaps, etc. Excellent protection was obtained by using either a kraft paper or a glassine soap wrapper prepared by the Riegel Paper Company, both treated with pentachlorophenol, and heavy kraft paper supplied by the Mosinee Paper Company also provided good protection. Other suitable papers may be available but have not come to the attention of the authors. Some commerically available papers contain mercurials but they have been avoided because mercury compounds are capable of bleaching the silver image and are presumably toxic.

(b) *Foil Envelopes.* Laminated aluminum foil of the type used for packaging sheet film is very satisfactory for making moisture-resistant negative storage envelopes. The foil itself is almost impervious to fungal attack and retains its bright, clean appearance for a long period. When hermetically sealed under dry conditions, aluminum-foil envelopes afforded excellent protection against fungus and fading, even to poorly washed negatives stored for one year on Barro Colorado Island. The use of heat-sealed foil envelopes does not seem entirely practicable for amateur or studio files where negatives are frequently handled and inspected, since it would, of course, be necessary to re-dry the negative and envelope every time the seal was broken. However, this system of protection might offer some advantage in the case of negatives intended for archival storage.

(c) *Interleaving Paper.* Interleaving paper was satisfactory when made of lighter-weight stock and more porous materials than the envelopes. They added materially to the protection afforded the negatives and were of special benefit when several negatives were stored together.

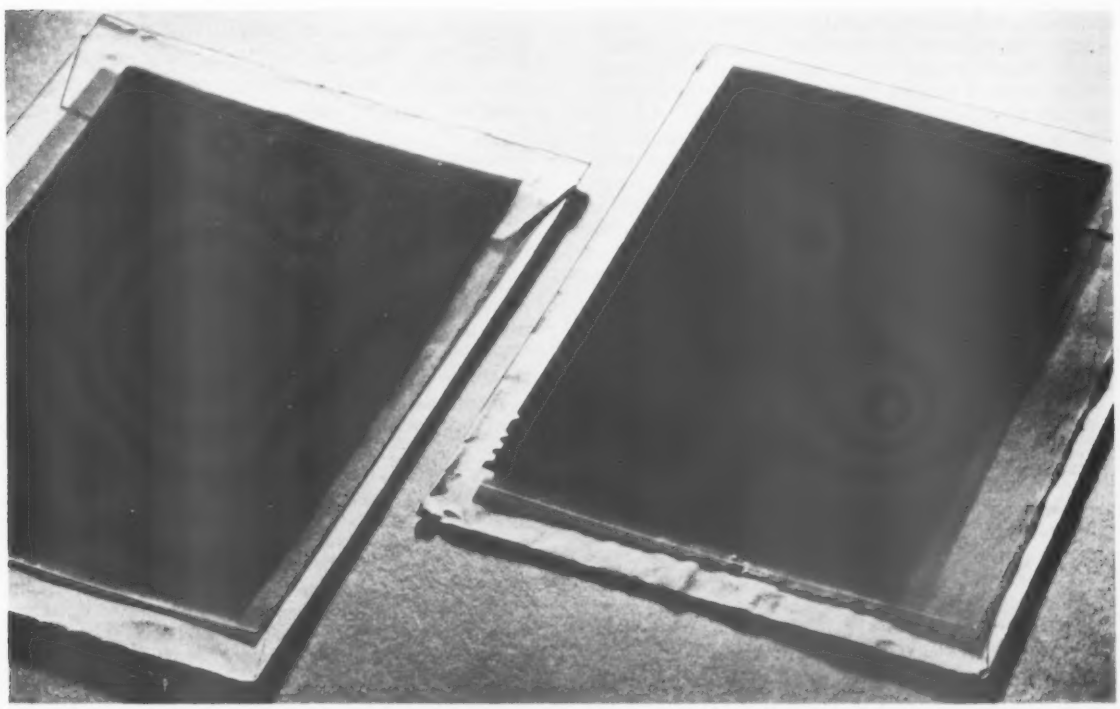

Fig. 3. Comparison of negative stored in an untreated envelope (left) with one stored in an envelope impregnated with the sodium salt of penta chlorophenol (right). Negative stored in the treated envelope is substantially free from fungus growth.

Format

An edge seam was found more desirable than a center seam. Negatives containing residual silver and hypo have been found to fade first along the seam, while the increased pressure in the seam area may permanently distort negatives squeezed together in a file.

The presence of a thumb hole has proved to be a weakness and fungus attack is likely to occur around the open edge of an unflapped envelope, both due to the weakening of the fungicide's influence and the chance introduction of nutrient matter. Conversely, a flap is very desirable.

Adhesive

Aqueous glues absorb moisture which increases the attack on the negative and causes local fading. They also are attacked by fungus and lose their adhesiveness on long exposure to moist conditions. The pressure-sensitive adhesive of certain cellophane tapes is attacked by fungi. Cellulose acetate cement (e.g., Kodak Rapid Mounting Cement) and vinylite cements, as well as a rubber-based adhesive, have proved very satisfactory.

The Fungicide

The sodium salt of pentachlorophenol (Dowicide G,* Santobrite†) was by far the best preservative (Fig. 3). Its effect varied from complete prevention of fungus growth to reducing it to light growth, depending considerably upon the nature of the paper. As already indicated, it was most effective in heavy, tightly woven papers and in glassine papers. Useful concentrations ranged from 1 to 2% as the aqueous solution in which paper was bathed, or 0.5 to 1.0% in the pulp. One commercial paper contained the copper salt; this was approximately equally satisfactory. We have avoided the use of the free phenol, as it is appreciably volatile and might be presumed to escape from the paper during a long period. We encountered no such loss of the sodium salt of pentachlorophenol, protection lasting through five to six years, even when exposed unprotected to the air.

Zinc fluosilicate did not act as efficiently as the pentachlorophenol salt in the treatment of envelopes. This compound is known to have toxic properties and its use should be avoided.

The quaternary ammonium compounds, Hyamines‡ 1622 and 3258, tended to absorb moisture and produced little net protection.

Zinc dimethyldithiocarbamate showed little fungicidal activity.

Dimethyldichlorosuccinate was an effective preservative in a glassine paper when used at high concentrations but proved to be toxic and difficult to handle.

Phenols—in addition to pentachlorophenol, e.g., Dowicide G, the following commercial phenols were tested but found less effective: Dowicide C, Preservagent, G-4, and Shirlan.

Application of the Fungicide

The most common method of application of the fungicide was to bathe the paper in a solution of the fungicide in water or appropriate solvent. This is very satisfactory for papers of reasonable wet strength and offers manufacturing advantages, if only a small portion of the paper produced by a manufacturer is to contain the fungicide. It is not suitable for glassine and low-wet-strength papers. In a few tests, the fungicide was added directly to the pulp during beating in manufacture. This procedure is used in the production of some commercially available papers.

Negatives Employed

The series of tests were confined to the Kodak Sheet Film negative materials, Super-XX, Tri-X, and Panchro-Press, Type B. These materials behave very similarly and tend to develop the earliest and most severe fungus on the pelloid and less in image areas, although fungus does develop here after some delay. The silver image discourages growth temporarily; this has been recently confirmed also for paper emulsions. The presence or absence of hypo did not make a great difference with regard to fungus attack. It has been observed that very hard emulsions, such as microfilms and roll films, are less readily attacked, and that soft emulsions, as in certain color products, are more readily attacked than the negative materials just mentioned.

Exposure Conditions

The rate of attack is increased with the severity of the exposure, as might be expected. Negatives hung on an open wire are attacked before negatives placed in untreated storage envelopes, and negatives in envelopes stored in a file drawer are attacked still more slowly. However, while changed storage conditions affected the rate of attack, they did not upset the relative effectiveness of the various methods of treatment.

Envelopes impregnated with the sodium salt of pentachlorophenol were exposed to sunlight, behind glass, for $2^1/_2$ years. Under these conditions, the pentachlorophenate decomposed, its protection was lost, and the negatives developed fungus. The photodecomposition of pentachlorophenol appears to involve the production of some di- and polyhydroxy derivatives of the phenolic compound, together with the release of chlorine.[1] This photochemical breakdown has little practical importance and it does not constitute a serious objection in this application, since intense solar radiation, particularly in the ultraviolet region, is necessary, and there was no evidence of loss under diffuse daylight.

* Registered trade mark of the Dow Chemical Co.

† Registered trade mark of the Monsanto Chemical Co.

‡ Registered trade mark of the Rohm & Haas Co.

1. I. A. Olivares, unpublished work.

Practical Recommendations for Storage Envelopes

The Paper

The paper should be heavy, nonporous, off-white, and possess high wet strength. It should be free from metal particles and ground wood pulp and be photographically inert. Good materials include 33- to 50-lb kraft (sulfate) paper and plastic-free glassine papers.

If there is doubt about its suitability, the paper may be subjected to the tests of ASA Standard PH4.20.

ASA Standard

The standard PH4.20-1958* describes suitable dimensions for storage envelopes and includes physical and photographic tests for their suitability. This standard has been revised to include the wider range of information obtained in tropical testing, including the tests just described. The inclusion of a fungicide is an optional feature.

Fungicide Treatment

The paper should contain 0.5 to 1.0% of sodium pentachlorophenate. Good grades of this commercial chemical are suitable. The fungicide may be added in the making process or by bathing the paper in a 2% aqueous solution.

Certain commercially available papers are suitable. At the time of these experiments, the Riegel Paper Co.† and perhaps others were in a position to supply kraft and glassine papers containing the specified quantities of fungicide. Mosinee‡ Permold Paper, Spec. 816, natural kraft, also contained a suitable fungicide.

Envelope Format

The envelope should employ the narrowest edge seam which the manufacturer can supply. This is usually about $^1/_2$ in. and should not be more. The envelope should have a flap $1^1/_4$ to $1^3/_4$ in. in width, depending on the size of the envelope. The adhesive should be nonhygroscopic and preferably nonaqueous. Vinyl and acetate cements are suitable. Both Kodak Rapid Mounting Cement and Swift's 1711-R adhesives have proved adequate. Rubber latex and polyvinyl acetate adhesives in a water suspension are also suitable and are reported to be easier to apply. Negatives should be stored with the emulsion side away from the envelope seam to minimize possible chemical reaction.

Interleaving Papers

These should be of adequate size to cover the negative completely. A folded paper is particularly recommended. The same comments apply to these as to the envelope papers except they may be of thinner and more porous paper. They will give added protection over and above that given by the envelope and are a necessity if more than one negative is stored in an envelope.

It is hoped that the results of these experiments, in conjunction with the ASA specifications, will serve as a guide to manufacturers of negative storage envelopes who may be interested in a special product for tropical and general use.

* Available from the American Standards Association, Inc., 10 East 40th St., New York 16, N.Y.

† Riegel Paper Co., 260 Madison Ave., New York 16, N.Y.

‡ Mosinee Paper Co., Mosinee, Wis.

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• Discussion and Evaluation

Eyepieces in Photography

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The selection of an eyepiece on the basis of magnification required, field of view and other factors is discussed. Design criteria and methods are reviewed, and it is suggested that the use of automatic computers should allow a re-evaluation of well-established eyepiece designs with a view to improving them by the use of aspheric surfaces or rare-earth glasses. American patents on eyepieces are tabulated.

Photography and photographic instrumentation have long required and used various types of magnifiers, oculars and eyepieces, either in magnifying an image in viewing instruments, or in measurement, alignment, viewfinders, rangefinders, photogrammetric instruments, perspective correction, etc. It is the aim of this paper to acquaint the user of eyepieces with the various characteristics of oculars so that he may better select and use them, and to present a tabulation of American eyepiece patents and designs of use to American designers.

The selection of an eyepiece of a given focal length is usually made on the basis of the magnification desired. The effect of magnification is to produce a larger image on the observer's retina. One may achieve this result by placing the eye closer to the object being viewed; however, the power of accommodation limits this technique. An eyepiece permits the eye to approach the object to within the lens's focal length since the lens renders the rays from the object less divergent. Assuming that the "normal" viewing distance is 10 in., then with an object at the focus one may compute the magnification from the formula:

$$M = 10/f'$$

where f' is the eyepiece focal length in inches.

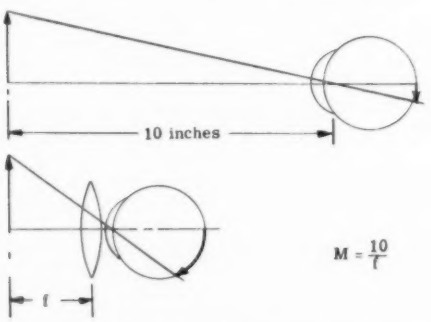


Fig. 1. Principle of eyepiece magnification. Use of an eyepiece permits the eye to approach an object more closely, producing a larger retinal image and apparent magnification.

Presented at the Annual Conference, Santa Monica, California, 13 May 1960. Received 14 April 1960.

It is possible to use an eyepiece in a manner such that the object falls inside the anterior focus, producing an image closer than infinity. When this image is formed at a distance of 10 in., one has gained an additional unit of magnification which may be calculated from the formula:

$$M = 10/f + 1$$

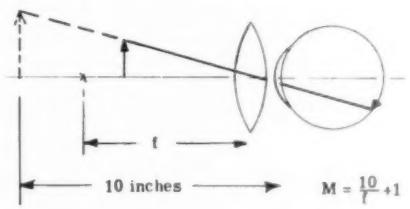


Fig. 2. Magnifier used for $10/f + 1$ magnification. An object may be placed inside the focus to form an image at 10 in., producing an apparent magnification of $10/f + 1$.

The magnification alone may be achieved by a simple convex lens of the proper focal length, provided one is interested in observing only a small area. In many instances, it is necessary to view larger areas requiring an eyepiece of large field. At other times, it may be impossible physically to locate the observer's eye close enough to the object and lens to permit viewing. An eyepiece having a long eye relief or eye clearance would

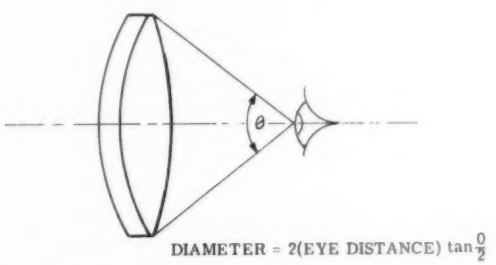


Fig. 3. Relationship of lens size to eye clearance and apparent field. The eye lens must subtend an angle equal to the apparent field of view and will increase in size with greater eye clearance.

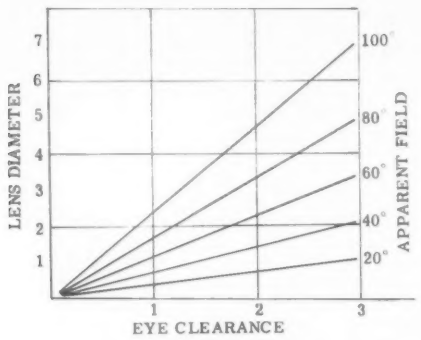


Fig. 4. Lens diameter vs eye clearance for various apparent fields.

permit a more remote eye location. The size of an eyepiece is very much dependent on the joint requirements of field and eye clearance, as may be seen in Fig. 3. From this figure it can be seen that

$$\text{Diameter} = 2 \times (\text{eye distance}) \times \tan(\theta/2)$$

Figure 4 shows a graph of the relationship between eyepiece size, clear eye distance, and apparent field angle. From this graph it is easily seen why wide-angle eyepieces requiring long eye clearances become so large.

One other determinant of eyepiece size is the anthropological characteristics of the human face, which limit the physical proximity of the eye to a given eyepiece. Figure 5 shows the envelope or locus of facial limitations which must be accommodated.

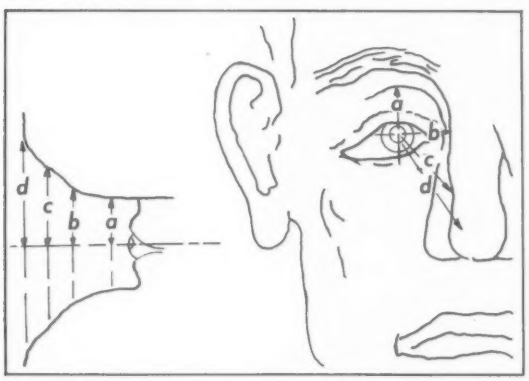


Fig. 5. Facial configuration and limitations. Features of the face may obstruct or limit the use of an eyepiece.

Selecting the optical design of an eyepiece is a more difficult problem since the choice depends on the intended use and tolerance of residual lens aberrations. It is common practice in the laboratory or shop to use a given eyepiece with various objectives or, *vice versa*, as a magnifier. This is a satisfactory practice, providing the limits of the eyepiece capabilities are not stretched; however, special requirements such as large fields, color correction, and freedom from distortion may require an optimum state of design correction. Aberrations to be corrected for eyepieces are the same as for camera lenses, namely: spherical aberration, distortion, coma, astigmatism, lateral

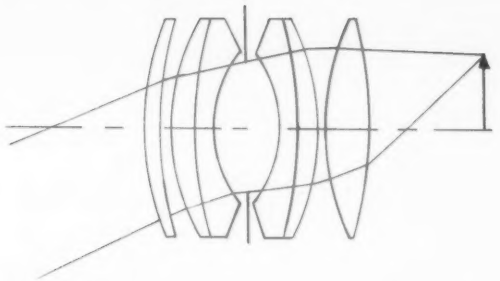


Fig. 6. Optical path through a typical photographic lens. Photographic lenses have centrally located aperture stops permitting a more symmetrical ray path.

color, longitudinal color, and field curvature. The correction requirements are usually similar, since both are used for producing flat image planes and require wide fields with minimum distortion. However, the very nature of an eyepiece and its use with the eye as the stop impose design difficulties. The stop, as stated above, is the pupil of the observer's eye and must be located at some distance from the lens, in contrast to the camera lens in which the stop is centrally located (Fig. 6).

Thus the rays from extra-axial images are made to traverse the eyepiece in unsymmetrical paths, causing inherent distortion, lateral color, and astigmatism. The eye pupil is usually small compared with the lens diameters, especially when large fields are to be used, and for this reason much positive power has to be placed at low ray height, resulting in large Petzval sums and field curvature. The small pupil size does, however, help to reduce the effect of spherical aberration and coma (Fig. 7).

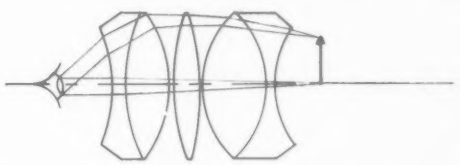


Fig. 7. Ray path through an eyepiece. The stop of an eyepiece is the observer's eye which requires an unsymmetrical ray path for extra-axial objects.

Eyepieces, when used in optical systems such as telescopes and microscopes, usually form a real image of the entrance pupil, and it is at this image point that the eye pupil must be placed in order to use the eyepiece properly. Should the eye and exit pupil not coincide, there will result an occlusion of various portions of the field. However, when an eyepiece is used as a magnifier there is no real pupil formed and the eye pupil may intercept rays that cause image deterioration when mispositioned; thus means must be provided for accurately locating and fixing the eye with respect to the lens (Fig. 8).

During the past decade automatic digital computers have become widely used for lens and optical system design. Prior to this it was necessary for the optical designer to perform tedious ray tracing, using logarithms or desk calculators. Consequently, many computational shortcuts and analytical methods were devised: for example, the stop shift theory of Conrady[1] and the use of

1. A. E. Conrady, *Applied Optics and Optical Design*, Dover Publications, New York, 1957.

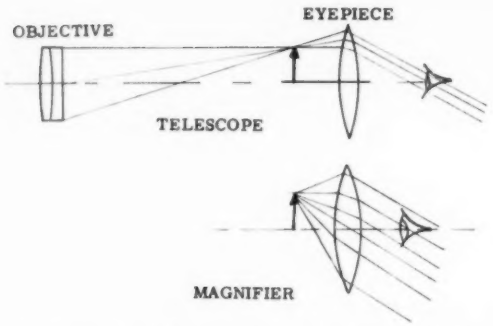


Fig. 8. Comparison of instrument eyepiece and magnifier. Instruments form real pupils fixing the eye location; magnifiers need a mechanical stop or head rest to fix the eye.

third-order Seidel aberration coefficients. Now automatic computers give exact ray traces through spherical surfaces in a matter of seconds while aspheric surfaces require only a little longer. Thus the lens designer can now obtain aberration data, make a change, and observe its effect in a matter of minutes. Automatic correction has been achieved,[2] although usually large amounts of storage are required for this type of programing. We at Nortronics use an automatic color correction program that permits a Conrady D-d correction[3] at a selected surface, thus insuring that the system being checked is always corrected.

It is strange, in the light of the above, that no greater advances have been made in eyepiece design during this period. This fact may indicate the excellence of prior designs and suggest that nothing better can be obtained. Only recently, however, the new rare-earth glasses have made an appearance in eyepiece designs, affording better correction at large fields. It is felt that further investigation of their use will lead to even better eyepieces.

It is possible to improve the state of correction very noticeably by using aspheric surfaces in eyepiece design. However, despite the designer's new-found capability to evolve these designs, it is still difficult for the shop to manufacture aspheric lenses, especially where critical curvature and large production quantities are involved. For this reason, the lens designer prefers conventional spherical lenses and attempts to achieve his correction by choices of glass.

Taylor, in his paper[4] on the evolution of the inverting eyepiece, presented a table of British and German patents for various types of eyepieces. Below is a similar tabulation of American patents and designs. As was suggested by Taylor, a further investigation of the aberrations of these eyepieces is in order. The author is performing this task with the aid of a digital computer and expects to publish the results in a future paper.

Most of the patents in the table are duplicates of European patents by German and English inventors. The notation used by Taylor is followed here; e. g., a 2-1-3 eyepiece consists of a doublet field lens, followed by a singlet, and a triplet eye lens. All eyepieces have been scaled and computed for a focal length of unity and the percent eye clearance is simply the ratio of the posterior focal length to the equivalent focal length.

2. G. Black, *Proc. of Symposium on Optical Design with Digital Computers, Technical Optics Section*, Imperial College of Science and Technology, London, June 1956.
3. A. E. Conrady, *Dictionary of Applied Physics*, Peter Smith, New York, 1950, p. 225.
A. E. Conrady, *Monthly Notices of the Royal Astronomical Society*, Jan. 1904, p. 182, Mar. 1904, p. 458.
4. E. W. Taylor, *J. Sci. Instr.*, **22:** 43 (Mar. 1945).

U.S. Patents for Various Types of Eyepiece Designs

Patent number	Type	Inventor	Date	Per cent eye clearance	Petzval sum	Field
1 468 762	1-3-2	Taylor	9–25–23	0.69	0.86	60°
1 478 704	2-1-2	Erfle	12–25–23	0.75	0.61	70°
1 479 229	2-2	Erfle	1–1–24	0.80	0.67	70°
1 759 529	1-3-1	Von Hofe	5–20–30	0.59	0.75	Large
1 759 529	2-3-2	Von Hofe	5–20–30	0.45	0.79	Large
1 968 222	1-3 (Aspheric)	Richter	7–31–34	0.43	0.74	60°
2 015 527	1-1-4	Konig	9–24–35	0.56	0.27	48°
2 206 195	1-2-1	Konig	7–2–40	0.62	0.77	60°
2 206 195	2-1-1	Konig	7–2–40	0.92	0.66	60°
2 206 195	3-2-1	Konig	7–2–40	0.68	0.78	65°
2 267 832	1-3	McCarthy	12–20–41	0.60	0.66	57°
2 394 635	2-2-2	Reiss	2–12–46	0.15	0.18	24°
2 419 151	2-1-2	Miles	4–15–47	0.38	0.46	75°
2 423 676	2-1-2	Altman	7–8–47	0.66	0.47	50° implied
2 549 158	2-1-1-2	Bertele	4–17–51	0.66	0.37	80°
2 549 158	2-2-1-1	Bertele	4–17–51	0.60	0.77	90°
2 621 564	2-1-1-2	Bertele	12–16–52	0.43	0.66	77°
2 637 245	1-1-3	Ludewig	5–5–53	1.37	0.23	42°
2 637 245	1-1-2-1	Ludewig	5–5–53	1.32	0.27	42°
2 637 245	1-1-1-2	Ludewig	5–5–53	0.78	0.38	90°
2 637 245	1-1-1-2	Ludewig	5–5–53	0.86	0.38	78°
2 637 245	1-1-1-2	Ludewig	5–5–53	1.36	0.39	42°
2 846 922	2-1-1-2	Kohler	8–12–58	0.87	0.24	60°

• Book and Journal Reviews

New Types of Photography Involving High Polymers

A Review Presented at Tokyo University, Japan, 18 March 1960, by Gerald Oster, Institute for Polymer Research, Polytechnic Institute of Brooklyn, N.Y.

The first successful photograph was produced with a polymeric substance. Niepce in 1822 obtained a photograph by exposing with outdoor illumination for 12 hr a glass plate coated with an asphalt, bitumen of Judea. The highly illuminated regions were rendered insoluble in solvents which normally dissolve the asphalt because the polymer had been crosslinked. Some modern versions of this phenomenon are the light insolubilization system of Kodak (a cinnamic acid ester of polyvinyl alcohol), that of Kalle (a diazonium salt with polyvinyl alcohol), and that of Time-Life (alcohol-soluble nylon suspension containing some unstated chemicals).

An early type of photography which is widely used today in practically its original form is the bichromate process. Fox Talbot, in 1852, demonstrated that gelatin containing a bichromate salt becomes insoluble after exposure to sunlight. In modern practice, one employs an aqueous solution of one of a number of high-polymeric materials (gum arabic, polyvinyl alcohol, gelatin, serum albumin, etc.) containing a few per cent of ammonium bichromate. The nature of the photochemical reaction is still not understood. One suggestion is that the chromium of valence 6 in bichromate is photoreduced by ultraviolet light to a salt of chromium of valence 3. This latter salt is known to crosslink certain high polymers to render them insoluble and, in fact, is used to tan leather.

Both these early 19th century discoveries were soon eclipsed by the discovery of the remarkable properties of silver halides, in particular their high light sensitivity and their ability to produce highly opaque images. Still later developments demonstrated that silver halides could be sensitized to visible light, whereas the polymer crosslinking reactions could only be carried out with ultraviolet light, using either sunlight or lamps of considerable power. Although the polymer systems have proven useful for photomechanical systems (e.g., photoengraving) they are of severely limited use in photography, particularly because of their insensitivity to visible light.

In our laboratory, we have discovered that polymers containing mercaptan groups can be crosslinked by visible light using dyes as sensitizers.[1] These dyes in the presence of suitable electron donors will sensitize the bichromate reaction, thus converting this method to a visible light process.[2] High polymers which have been crosslinked by metal ions can be sensitized so as to collapse, i.e., lose their gel characteristics by exposure to visible light.[2] A quite different approach is to sensitize the polymerization of vinyl monomers with dyes.[3] I should like now to describe actual photographic systems based on these phenomena. First, however, we should review the photoreduction of dyes upon which all the phenomena mentioned above are based.

Photoreduction of Dyes

Many dyes in the presence of electron donors will undergo reduction when illuminated by visible light. Such dyes include, for example, members of the thiazine and fluorescein families. The reducing agent can be any one of a wide variety of mild reducing agents, including allylthiourea, ascorbic acid, cysteine, etc. Many chelating agents, including ethylenediamine tetraacetic acid (EDTA), also serve as electron donors for the light-excited dye molecule, although such agents are not normally regarded as reducing agents.

In the usual case, the light-excited dye molecule undergoes a transition to a long-lived state which is the chemically reactive species.[4] In other cases,[5,6] particularly for dyes bound to high polymers, a dye molecule in the ground state may interact with an excited dye to induce it to undergo a transition to the long-lived state.

The photoreduced dye thus produced can be a strong reducing agent. In the case of proflavine, for example, the reduction potential of the reduced dye may be as low as -1.3 v.[7] For most other dyes, the reduction potentials lie between 0 and -0.5 v.[7]

The rate of photoreduction of the dye is dependent on the amount of electron donor present. For thiazine dyes, the quantum yield for photoreduction may be close to unity[8] but is generally smaller than this value for other dyes.

Dye Sensitized Photocrosslinking of Thiol Polymers

When the reducing agent used with the dye is a thio compound such as cysteine, glutathione, mercaptoethanol, etc., the illuminated system contains reduced dye and the disulfide. The oxidation involves the participation of two thiol molecules. Oxidation may also proceed by dye-sensitized photo-autooxidation, which is related to the photoreducibility of dyes.[9] If the thiol groups are residues of macromolecules, the photoreduction can thus result in crosslinking.

In our studies, we have employed thiolated gelatins containing from 5 to 20 thiol groups per 10^5 grams of polymer. Some photoreducible dye, such as erythrosin, is added to the gelatin solution, and the system is allowed to set. On exposure to visible light, the light-struck portions are rendered insoluble in hot water. In fact, the crosslinked polymer remains clear and intact even after prolonged immersion in boiling water. Thioglycollic acid will, however, readily dissolve the crosslinked polymer, as one would expect.

The system shows promise as a photomechanical system which is sensitive to visible light for the produc-

1. G. Oster and G. K. Oster, Int. Symp. Macromolecular Chem., Moscow, June 1960.
2. G. K. Oster and G. Oster, *J. Am. Chem. Soc.*, **81:** 5543 (1959).
3. G. Oster, *Nature*, **173:** 300 (1954).
4. G. Oster and A. H. Adelman, *J. Am. Chem. Soc.*, **78:** 913 (1956).
5. G. Oster and J. S. Bellin, *ibid.*, **79:** 294 (1957).
6. F. Millich and G. Oster, *ibid.*, **81:** 1357 (1959).
7. G. K. Oster, G. Oster, and E. Schatz, to be published.
8. G. Oster and N. Wotherspoon, *J. Am. Chem. Soc.*, **79:** 4836 (1957).
9. G. Oster, J. S. Bellin, R. W. Kimball, and M. E. Schrader, *ibid.*, **81:** 5095 (1959).

tion of color plates working directly from color transparencies.

Dye Sensitized Bichromate Process[2]

The reduced form of the dye can reduce a wide variety of ions, including bichromate ions. One cannot use ordinary reducing agents as the electron donors, since then the bichromate ion would be reduced in the dark. With chelating agents, however, this difficulty is overcome.

A gelatin solution containing bichromate, a dye such as methylene blue, and a chelating agent such as EDTA is allowed to gel. On exposure to visible light (red light in the example chosen), the gelatin is rendered insoluble. This reaction appears to be far more sensitive than the ordinary bichromate process and besides being of use for direct color-plate production (using a single-color negative) could also be used in enlarging and in reflex copying cameras.

Dye Sensitized Photo-Decrosslinking[2]

Many water soluble polymers form complexes with metal ions. If this complexation occurs intermolecularly, then a crosslinked gel is obtained. This is the case, for example, with polyacrylamide in the presence of mercuric ions. The gel thus obtained is optically clear, tough, and nonswelling in water. The gel, if sensitized with a dye and a chelating agent (triethanol amine, for example), collapses on illumination with visible light. The photoreduced dye reduces the mercuric ion to mercurous ion. This latter ion does not serve as a crosslinking agent, so that the gel is decrosslinked and hence becomes soluble in water.

The action of visible light in causing the collapse of a gel is unique in the field of photography, and offers some interesting possibilities for direct color photography. Suppose one were to make a three-layer system of the mercuric gel with chelating agent, one layer with a cyan dye, one with a magenta dye, and one with a yellow dye. The total appearance is black. On exposure to red light, the cyan layer collapses and can be washed away with water. The system then appears red. On exposure to green light, the magenta layer collapses and the system appears green, and so on. In this manner, a faithful color reproduction is produced. The washing with water not only removes the collapsed polymer but also removes the chelating agent necessary for the reaction, and hence the image becomes fixed.

Dye-Sensitized Photopolymerization[3]

Reduced dyes can react with oxygen to produce free radicals. The free radicals are readily detected by their ability to initiate polymerization of vinyl compounds. That oxygen is playing a role in the reaction is demonstrated by the following experiment: if a system containing dye, electron donor, and monomer, scrupulously freed of oxygen (by bubbling very pure nitrogen through the solution), is irradiated, the dye is photoreduced, but no polymer is produced. If oxygen is allowed to enter the irradiated system, however, polymer is formed. Hence the reaction appears to be initiated by radicals produced in the reaction of reduced dye and oxygen.

The polymerization reaction is extremely rapid and quantum yields exceeding 10^6 are possible.[10] The induction period, however, imposes a limitation on the over-all speed. If this were overcome, one would have a photography as fast as that of silver halide photography. Even in its present state, dye-sensitized photopolymerization shows considerable promise as a remarkably simple and convenient type of photography. The image is formed during the exposure, and fixation consists simply in inactivating or removing any one of the reacting components. For direct visualization, one may use a divinyl monomer to give a highly crosslinked light-scattering image.

A number of photographic systems have been made using dye-sensitized photopolymerization. For example, a plastic printing plate can be made directly from a camera shot. We have also made a photosensitive mimeograph master (this gives a positive from a positive), a lithographic plate, and a diffusion transfer paper. All these systems are quite sensitive to visible light and may form the basis of one or another color process.

Conclusions

There are four important features of the systems described here, namely: (1) their sensitivity to visible light; (2) their high effective quantum yield; (3) the sharpness, i.e., high resolution, of the produced image; and (4) the enormous difference in physical properties between the exposed and the unexposed regions.

The spectral sensitivity of these systems is dependent on the color of the dye employed. For example, methylene blue used as the sensitizer renders the system susceptible to the red-orange region of the visible spectrum only. With silver halides, on the other hand, the spectral sensitivity of the system is determined by the absorption spectrum of the silver halide as well as that of the bound sensitizing dye. Far ultraviolet light will also cause many of the changes which we have described. For example, far ultraviolet light will degrade, by breaking crosslinks, polymeric systems which are crosslinked by titanic ions[2] (as with polyvinyl alcohol) or by disulfide linkages (as with thiolated gelatins).[1] On the other hand, such polymers as polyethylene can be crosslinked by far ultraviolet light if a sensitizer such as benzophenone is employed.[11]

The high effective quantum yield is achieved by the fact that macromolecules or chain reactions are involved. With a plastic of molecular weight 10^6, only 10^{-5} moles of crosslinks are required per gram of material to render it insoluble and infusible. If the quantum yield for the production or destruction of crosslinks by visible light is unity, then about one joule of radiant energy must be absorbed in a gram of the plastic to bring about the required change. For highly absorbing dye-containing systems, a gram of plastic can be spread over a square meter to give a 100% light-absorbing surface. Thus to effect the required change, the order of a millisecond exposure to sunlight is sufficient. This is a far cry from Niepce's daylight exposures of 12 hours!

In order to produce a sharp image by our method, it is essential that the image does not wander and the dark reaction does not extend beyond the boundaries of the exposed regions. We have found that the produced image does not wander appreciably because the diffusion constants of macromolecules are quite low. There is no detectable wandering with images produced by photopolymerizing divinyl compounds. On prolonged ex-

10. G. Oster, G. K. Oster, and G. Prati, *J. Am. Chem. Soc.*, **79**: 595 (1957).

11. G. Oster, G. K. Oster, and H. Moroson, *J. Polymer Sci.*, **34**: 671 (1959).

posures, however, such images scatter light during the exposure so that the image can become diffuse and extend beyond the boundaries of the initially exposed regions. Dark reactions can proceed for long periods of time as, for example, in post-polymerization processes in viscous media.[10] Although images do in certain cases intensify after the light is removed, the image seems to be confined entirely to the exposed regions. We have exposed some of our systems through very dense halftone printing screens and have established by microscopic examination of the image that resolutions of better than 10 μ are achievable.

In all systems we have considered, drastic physical changes take place when the system is illuminated. These may involve the transformation from a clear film to a highly light-scattering image. This is the case, for example, when a divinyl compound is photopolymerized. Incidentally, here the image is positive when viewed against a black background and negative when viewed by transmission of light. Changes in solubility are particularly striking, and most of our methods for making the image visible are based on this change in property. In our gel-collapsing system, the release of pigment can be quite impressive. We must admit, however, that with the possible exception of the scattering image, it is difficult to achieve directly the high black-and-white contrasts which are achievable in silver halide photography. We have, however, been able to improve even the high density of silver halide images with monomers which polymerize by the action of the free radicals produced during the oxidation of conventional photographic developing agents.[12] This action produces polymer which aggregates only those silver halide granules that have been light struck and therefore are developable. If the silver granules are in the correct size range, such aggregation will result in an increased optical density of the image and thus an over-all increase in sensitivity of the photographic emulsion will be achieved.

12. G. Oster, *Nature*, **180:** 1275 (1957).

Keemag Graphic Solutions in the Use of Lenses

JOSEPH D. BRUBAKER, published by Joseph D. Brubaker, 949 Sherman Ave., Evanston, Ill., 50 pp., 2 calculator dials, $15.00

Keemag Graphic Solutions in the Use of Lenses is a manual containing a system of graphs, charts, scales, dials, tables, diagrams, and reference data for direct graphic use. Apparently no new ideas or data are contained in this manual; the material used is now scattered among several reference books, and the idea of coordinating all of it under one cover is very good. The manual should prove useful to those who are interested in locating this information quickly.

Potential users of this manual will be found in many branches of the photographic field (from the designers of photographic equipment to the copy photographers), and also in many fields outside of photography where optics play a part (such as astronomy, rangefinder work, television, and others.)

A person who encounters optics problems only occasionally can probably solve his needs more quickly by solving formulas or equations rather than by learning to use a complex graph, and a person who has a special problem which he must solve repeatedly and often probably will have his own method of solution which he can use with great efficiency. The manual should be of greatest benefit to someone whose work involves a wide variety of problems and frequent lens calculations; it should also be helpful for classroom instruction in optics. —*John W. Gosling, Eastman Kodak Co.*

First Conference on the Spectroscopy of Light-Scattering Media

Held in Moscow, March 29–30, 1956

All but four of the papers presented at this Conference have been published in Vol. 21, No. 11 (1957) of *Izvestiia Akad. Nauk USSR, Ser. fiz.*, an English translation of which (*Bull. Acad. Sci. USSR, Physical Series*) is published by Columbia Technical Translations, 5 Vermont Ave., White Plains, N.Y. ($20 for single issues). The following papers deal with photographic materials: *Light Scattering Index for Developed Photographic Emulsions on a Transparent Base*, YU. N. GOROKHOVSKIĬ AND I. M. DAVYDKIN, pp. 1496–1506; *Numerical Evaluation of Light Scattering in Photographic Blackenings on a Transparent Base*, —— AND ——, pp. 1507–1514 (see *Phot. Sci. & Eng.*, **3:** 150 (1959) for an abstract of a paper by the same authors based on the same material); *Scattering of Light by Photographic Emulsion Layers*, P. KH. PRUSS, pp. 1515–1521 (see *Phot. Sci. & Eng.*, **4:** 60 (1960)); *Procedure for Investigating the Reflectivity of Color-Print Photographic Papers*, V. M. BAKHVALOV, pp. 1522–1527.

Bakhvalov concludes: "Two basic conditions must be borne in mind in designing attachments for spectrophotometers for the purpose of measuring the reflection curves of photographic paper. (A) The angle of incidence of the light on the sample must be confined to the range from 0° to 40–50° to the normal since at higher angles the surface reflection rises sharply. (B) The observation angle should not be less than 15° with respect to the direction of mirror reflection."—*T.H.J.*

Scientific Publications of the Fuji Photo Film Co., Ltd.

No. 4, 1934-1952 (published December 1959).

SHIN FUJISAWA, Editor, distributed by Maruzen Co., Ltd., Tokyo, 131 pp., paper cover, $1.50.

The *Scientific Publications* brings together under one cover papers published over a specified period by the personnel of the Research Department of the Fuji Photo Film Co., Ltd. Issue No. 1 contained papers published during 1953, No. 2 during 1954, and No. 3 during 1955. No. 4, which appears after a lapse of several years, coincides in time with the 25th anniversary of the founding of the Company, and is made up of papers and abridgments of papers published between 1934 and 1952. Many of these papers appeared originally in early issues of the *Journal of the Society of Scientific Photography of Japan*, almost unobtainable in this country, or were presented at scientific meetings but apparently not published.

Issue No. 4 contains 19 original reports in Japanese, with abstracts, tables, and captions of figures in English. With the aid of the English portions, the reader who does

not understand Japanese still can often glean much information from the papers. Four of the papers deal with the preparation of sensitizing dyes, two with color couplers, two with the fading of silver images caused by residual thiosulfate, and two with the construction of sensitometers; others are on the action of 5-bromobenzotriazole in emulsions, hypersensitizing by exposure, the effect of corpuscular radiation on photographic emulsions, recovery of components from waste fixing solutions, a camera for testing resolving power, a meter for measuring silver ion concentration, coating of glass to reduce two-layer reflection, and the chemical composition of commercial emulsions. The paper on the last subject gives the silver, gelatin, silver iodide, silver bromide, soluble bromide ion, and soluble chloride ion contents of 15 photographic emulsions of Western manufacture. In addition, the issue contains the complete Japanese version of a review article on the use of photographic plates in spectrographic analysis, originally published in 1948, and 22 abridgments, in both English and Japanese, of papers published during the period 1936–1947. —*T. H. J.*

Journal of the Society of Scientific Photography of Japan

Vol. 22, No. 3, September 1959 (in Japanese)

Résumés by S. Kikuchi and T. H. James

Mourn Over the Death of Our Honorary Member, Prof. L. P. Clerc

SHINICHI KIKUCHI (Univ. Tokyo), p. 113, with full-page portrait

Progress of Photography in 1958

SHIN FUJISAWA (Fuji Photo Film Co., Ltd., Minamiashigara-machi, Kanagawa Pref.), pp. 114–120

A Developing Machine for Sensitometric Work

EIICHI MIZUKI, GORO AKASHI, HARUHIKO IWANO, SEIICHI TAGUCHI, AND REIJIRO FURUSAWA (Fuji Photo Film Co., Ltd., Minamiashigara-machi, Kanagawa Pref.), pp. 121–128

Control of temperature and agitation are of great importance in the design of a developing machine for processing sensitometric strips with a high degree of reproducibility. From considerations of the known temperature dependence of development, it was concluded that the variation in density caused by a variation of 0.2°C would be only 2.1%. A study was made of the effect of the design of various rotors upon the efficiency of the agitation obtained with them, and a rotor with spiral stirrers on its periphery was chosen as most efficient. The disturbance of agitation caused by projected bodies in the solution and by perforations on the film strips also was considered. On the basis of these studies, a machine was constructed in which the film strips were attached vertically to the interior wall of the cylindrical developing tanks and the agitation was supplied by rotors with two to four spiral folds mounted concentrically in each developing tank and driven by a motor. The direction of rotation was reversed at specified intervals during operation. The temperature was controlled thermostatically to ±0.1°C. The deviation in density of 12 strips developed in the machine was less than 2%. The quantities of solution needed were 600 cc for film of small size and 1100 cc for film of large size.

Two other types of developing machines were constructed, one for development of doubly coated x-ray film and the other, of large capacity, capable of developing 72 strips simultaneously. Schematic diagrams of all three machines are given. Tests made with singly coated film showed no difference in the quality of performance of the three machines.

Research on the Rapid Processing of Oscillograph Paper

GORO MIYAMOTO AND TOSHIO MIYAGAWA (Tokyo Junior College of Photography), pp. 129–138

This paper describes researches on the rapid processing of oscillograph paper with automatic rapid daylight processing machines. The machines contain a number of rollers, the lower parts of which dip into the developer. The oscillograph paper is moved on the surface of the rollers by a motor drive. The processing formula used with the cardio-type paper was: water, 700 ml; sodium sulfite, 45 grams; 1-phenyl-3-pyrazolidone, 1.1 grams; Metol, 15 grams; hydroquinone, 15 grams; sodium hydroxide, 60 grams; and water to make 1000 ml. The developing time was 2 sec at 20°C. The fixer consisted of 230 grams of ammonium thiosulfate crystals dissolved in water to make 1000 ml, and required about 60 sec at 20°C for complete fixation. The processing time was considerably shortened for certain types of chlorobromide paper. The developer was a modified version of the preceding (with only 30 grams of sodium sulfite and 0.9 gram of 1-phenyl-3-pyrazolidone) and required 2 sec; the fixer was the same and required only 12 sec. An experimental chlorobromide paper with a thin emulsion layer was prepared and tested. This material developed in 2 sec and required only 5 sec for fixing.

Studies of the Photographic Pressure Effect. IV. Influence of Chemical Sensitization on the Pressure Effect

YOSHICHIKA KOBAYASHI (Konishiroku Photo Ind. Co., Ltd., Tokyo), pp. 134–138

In this paper, Dr. Kobayashi reports the results of an investigation of the influence of the type and degree of chemical sensitization upon the magnitude and sign of the pressure effect. He prepared silver bromide emulsions of the neutral type, containing 2 mole % silver iodide, with gelatin which had been inactivated by treatment with hydrogen peroxide according to the recommendation of Kelly (*J. Phot. Sci.*, **6**: 16 (1958)). Some emulsion samples were sulfur sensitized to different degrees by sodium thiosulfate, others were given both sulfur and gold sensitization. The pressure was applied by bending the film strips before exposure to light. A *p*-hydroxyphenylglycine developer without sulfite was used to determine surface latent image; D-19 with the addition of 10 grams of sodium thiosulfate per liter was used to determine total and internal latent image. "Internal images" were determined for strips which had been bleached in 0.2, 0.5, 2, and 5% solutions of CrO_3.

The sensitivity of the emulsion prepared without chemical sensitization and of the sulfur-sensitized emulsions was decreased by pressure, for both surface and internal latent image formation, although the degree of desensitization for surface image formation became smaller with increasing duration of sulfur sensitization. The sensitivity of the sulfur-plus-gold sensitized emulsions was decreased by pressure for surface latent image formation. At low degrees of chemical sensitization, the sensitivity for internal image formation also was decreased by pressure, but at higher degrees of chemical

sensitization the sensitivity for deep internal image formation was increased by pressure.

The dependence of the pressure effect upon the intensity of the exposing light was determined for the sulfur sensitized emulsions. Pressure caused desensitization for surface image formation over the entire range of intensities (exposure times from 0.002 to 500 sec). When the emulsion which had a relatively low degree of sulfur sensitization was incubated at 50°C before exposure to light (no pressure), the surface sensitivity increased. When the incubation followed the application of pressure, the sensitivity to high and moderate intensity light exposure increased even more (pressure sensitization), but the sensitivity to low intensity light did not increase as much (pressure desensitization). Internal image formation was sensitized by pressure at all intensities for the incubated film. The emulsion which had been sulfur sensitized to the optimum lost sensitivity to high and moderate intensity exposures upon incubation, and pressure caused desensitization for all exposure intensities.

Further tests were made in which the emulsion prepared without chemical sensitization was subjected to pressure and then immersed for 15 min in a 0.01% sodium thiosulfate solution to etch the surface. The emulsion was then rinsed and dried before exposure. Both surface and internal sensitivities were increased by the pressure.

Psychophysical Treatments of Photographic Optics. II. Aspect Ratio of Pictorial Photographs

MINORU TAMURA (Chiba University, Matsudo-shi, Chiba Pref.), pp. 139–143

The aspect ratio (ratio of width to length) was determined for 8919 photographs and paintings which were classified according to the format of the original (35mm cameras, 6 by 6-cm cameras, other cameras) and subject matter (Western and Chinese paintings, female portraits, landscapes). Frequency distribution plots of the aspect ratio are given for the six categories and for the sum total. The mean aspect ratio is 1.38. The ratio of the number of horizontal photographs to vertical photographs is 2.6 for 32321 samples examined, but is only 0.77 for artistic photographs made by advanced photographers.

Studies on the Light Polarizer. I. One-Way Filter

TSUTOMU YODA, HIROSHI NAKAMURA, AND HEIZABURO IDE (Ofuna Factory, Mitsubishi Electric Mfg. Co., Ltd., Ofuna, Kamakura-shi, Kanagawa Pref.), pp. 144–150

The one-way filter consists of a circular polarizing element composed of a polarizer and a quarter wave plate. The materials, construction, properties, and accuracy of production of the filters and their application to reflection and transmission control are discussed.

Nuclear Emission Technique. I

AKIRA HIRATA (Konishiroku Photo Film Co.), pp. 151–160

A review is given, including tables and graphs which give: percentage of moisture contents of Ilford nuclear emulsions at various relative humidities; the percentage composition by weight of Ilford, Agfa, Konishiroku, and Kodak emulsions; maximum detectable energies of various emulsions; temperature variation of sensitivity; surface fading rates in Ilford C2 nuclear emulsions stored in various atmospheres at constant humidity; grain density vs energy loss rate for electrons in Kodak NT4 and Ilford C2 and G5 emulsions; range-energy curves for various types of nuclear particles in nuclear emulsions; and stopping power vs energy curves for protons and alpha particles in nuclear emulsions.

Technika Kino i Televideniya

Vol. 3, December 1959

Résumés by S. C. Goddard

Some Factors in the Plasticizing Process of Cellulose Triacetate Cinefilm

L. V. ROZENTAL', M. I. MUMZHIEV, Z. K. AVERBUKH, AND A. F. MUKOVNINA, pp. 12–17

The brittleness of triacetate film compared with that of nitrocellulose film is a problem which is aggravated by the difference in shrinking properties; the difference between the shrinkage of the emulsion layer and the relative lack of shrinkage of the triacetate film sets up stresses in the latter. A range of plasticizer has been studied and it is concluded that plasticizers based on esters of the higher fatty acids with from 6 to 10 carbon atoms in the acid radical and from 1 to 9 in the alcohol radical are compatible with partially hydrolyzed fibrous cellulose triacetate in the quantities necessary for lowering the brittleness of the base. To some extent the compatibility depends on the temperature and relative humidity. The structure of the alcohol radical is important: with a given number of carbon atoms in the acid radical, plasticizing action improves with increase in the number of carbon atoms in the alcohol radical.

The Calibrated and Uniform Application of Processing Solutions to Continuously Moving Film

S. M. LEVI, N. J. MASLENKOVA, AND N. I. KIRILLOV, pp. 18–25

Consideration is given to the fundamental conditions which ensure a calibrated and uniform application of processing solutions to a continuously moving film. On the basis of the derived equations, it is shown how the volume of a solution applied to the film depends on different factors arising in the use of different types of apparatus with dip-coating rollers, transfer-coating rollers, etc. The action of wetting agents in the application of processing solutions to the continuously moving film is considered, and the conditions are indicated for obtaining their uniform distribution over the surface of the film. In the experimental part of the paper, a study is made of the action of different wetting agents on the uniformity of application of developing and fixing solutions to the film. (*Translation of authors' abstract*)

Referativnyĭ Zhurnal, Fizika

(*The following are translations of abstracts appearing in this Russian abstract journal. The original sources generally were not available for comparison.*)

Translations by S. C. Goddard

A Study of the Absorption Spectrum of Internal Centers in the Infrared Region for Fine-Grain Silver Bromide and Silver Chloride Emulsions

E. A. KIRILOV, E. A. NESTEROVSKAYA, AND A. B.

GOL'DENBERG, *Pratsi Odes'k. Univ. Ser. Fis. Nauk.*, **148**:15–17, No. 6 (1958) (in Ukrainian)

The absorption spectra have been studied for surface and deep centers in crystals of fine-grain silver chloride and silver bromide emulsions in the range 800 to 2000 mμ. Plates with the emulsion to be studied, after exposure to a mercury lamp, were subjected to treatment with an oxidizing agent to eliminate the surface centers; other plates not treated after exposure served as comparisons for the study of surface centers. Absorption spectra obtained by differential spectrophotometry of relatively unexposed plates exhibited the following: (1) the absorption of the internal centers extended far into the infrared region up to 1400 to 1500 mμ; (2) a clearly marked fine structure in the absorption of both deep and surface centers; (3) approximately the same positions for the absorption maxima for both groups of centers and both silver salts; (4) with increase in wavelength the absorption of the surface centers decreases monotonically while that of the internal centers passes through a maximum at 1100 mμ for silver bromide and 1000 mμ for silver chloride. [*Translator's note:* In the absence of context, the phrase "glubinnŷe tsentrŷ" has been translated as "deep centers," but "sub-surface centers" might be more appropriate.]

A Spectral Investigation of the Absorption of Surface and Internal Centers in Coarse-Grain Silver Bromide Emulsions

A. B. GOL'DENBERG, *ibid.*, pp. 19–23

A study has been made of the absorption spectrum (400 to 1200 mμ) of a coarse-grain silver bromide emulsion of average sensitivity (16 GOST units) for purposes of comparison with results obtained earlier for fine-grain emulsions of low sensitivity (preceding abstract). Several relations were discovered which were general for emulsions with crystals of any size: the presence of a fine structure in the spectrum, the approximate coincidence of the position of the maxima of the internal and surface centers of a given emulsion on the one hand, and in emulsions with different degrees of dispersity on the other. In the case of coarse-grain emulsions, the magnitude of the absorption of light by internal centers is close to that for surface centers, while in fine-grain emulsions, the first magnitude is an order lower than the second. (*Slight abridgment of original.*)

A Study of Formation of Light-Absorption Centers in Exposed Silver Bromide at Low Temperatures

T. YA. S'ORA AND A. G. GUMENYUK, *ibid.*, pp. 25–27, No. 6, 1958 (in Ukrainian)

The differential method has been used to measure the subsidiary absorption of thin layers of fine-grain silver bromide emulsion in the spectral range 250 to 800 mμ, the exposure to an ultraviolet mercury lamp being made at temperatures from +20 to −163°C. In all cases, two wide bands were observed in the visible part of the spectrum (maxima at 405 and 530 mμ) and one in the ultraviolet region; the maximum of the latter region lies beyond the limits of the range studied and its existence can only be spoken of hypothetically on the basis of the monotonic increase in the ultraviolet region past 350 mμ. Both bands in the visible region decrease sharply with decrease of temperature and at the lowest temperatures obtained (−163°C) practically completely disappear; consequently the centers responsible for these bands arise in significant numbers only at temperatures allowing the migration of silver ions. The band in the ultraviolet region is less sensitive to temperature and at −163°C is still pronounced.

Equivalent Quantum Efficiencies of Photographic Emulsions

R. FELLGETT, *Ingénieur chimiste*, **40**:94–105, 224–233, 285 (1958) (in English)

The equivalent quantum efficiency, ϵ, of a receiver is defined as the ratio of the number of quanta, N, necessary to obtain the given information to the number, Q, actually absorbed by the given receiver for the same purpose. If, for the incidence of Q quanta, the ratio of signal to noise is R, than $N = R^2$ and $\epsilon = R^2/Q$. If the signal is recorded on the negative in the form of a density, D, with an average quantum fluctuation (noise), ΔD, then $R = \gamma/\Delta D$, and to a region of area, A, it is necessary, to communicate $N = (1/A)/(\gamma/\Delta D)^2$ quanta. Then ϵ is easily found if Q is known in absolute units of energy. For four Eastman Kodak emulsions used in astronomy, the dependence of N and ϵ on the exposure has been calculated for two wavelengths (430 and 607 mμ) on the basis of sensitometric and granularometric data. As the exposure is increased, both quantities pass through a maximum, with ϵ always at lower values than N. The maximum of ϵ is reached at exposures corresponding to $D \sim 0.1$ to 0.2 above fog, and has a value of the order of some tens per cent; this agrees with the calculation of R. C. Jones (*P S & E*, **2**:57 (1958)) for the same emulsions, carried out by a somewhat different method.

The Relation Between the Resolving Power of the System: Objective—Photographic Emulsion and the Relative Aperture of the Objective

V. BLUMOVÁ, *Československ. Časop. Fys.*, **8**:545–553 (1958) (in Czech)

An experimental determination has been made of the relation between the resolving power, R, of two photographic emulsions and the relative aperture, $1/c$, for a few moderately fast objectives (c greater or less than 3.5), the wave aberrations of which were determined previously in relation to $1/c$ by an interferrometric method. All measurements of R were carried out in monochromatic light of 5391 A. The value of $1/c$ for obtaining the highest value of R in all combinations of objective and emulsion corresponded to wave aberrations of less than $\lambda/4$, thus allowing the calculation of an objective which was physically perfect. However, the passage of R through a maximum at fairly high values of $1/c$ does not correspond to the theoretically calculated relation, which is a monotonous growth to a constant value. As a supplementary investigation has shown, these departures from theory are connected with deterioration in the quality of the image at large values of $1/c$. When this factor is correctly taken into account, no fall in R is observed and agreement between theory and experiment is restored.

Sensitivity and Regression of Silver Bromide Nuclear Emulsions

J. KUBAL, J. BENEŠ, AND Z. HRKAL, *Československ. Časop. Fys.*, **9**:133–140 (1959) (in Czech)

A study has been made of the effect of the addition of silver iodide (0-8 mole per cent) on the sensitivity,

S, of silver bromide nuclear emulsions containing cadmium bromide (for improving the dimensional uniformity of the grains). The emulsions were exposed to light and to α- and β-particles (α from Po-210 and β from C-14). The introduction of silver iodide up to 3% increases S in relation to light and to α-particles. Further increase of the concentration of silver iodide began to lower S to light, but, after 5.5%, S increased again. To β-particles, S was constant up to 3% silver iodide, then dropped, and, after 5.5% became constant again. In individual particle tracks with concentrations of silver iodide greater than 4%, an increase in grain size was noticed corresponding to a worsening of discrimination. Sensitization by 2-*p*-dimethylaminostyrylbenzothiazole (I) increased S (to light more than to particles), but had no effect on the character of the relation between S and the concentration of silver iodide. A study was also made of the rate of regression on the same emulsions at temperatures of 4° and 18°C. After sensitization by I, regression increased for the action of light and decreased for the action of particles; this rule does not depend on the presence of silver iodide in the emulsion. To explain this, it is suggested that I acts only on the surface development centers, the number and size of which are different for light and for particles. The rate of regression for silver iodobromide emulsions is less than that for pure silver bromide emulsions, while for the action of α-particles it is substantially less than for the action of electrons. Hypersensitization with triethanolamine after I significantly increases S to electrons: a low-speed nuclear emulsion acquires the ability to record separate β-particle tracks from C-14, while the speed S, estimated for a density of 0.6 above fog, increases more than ten times.

Measurement of the Resolving Power of Photographic Emulsions

I. Šolc, *Jemná Mech. a Opt.*, **4**:86–88, No. 3 (1959)

Resolving power of photographic emulsions is measured by photographing a Fresnel zone plate in monochromatic light onto the emulsion to be studied. In the Fresnel zone plate, there is a regular decrease in thickness of the light and dark rings with the increase in diameter of the rings, and this makes it easy to find the resolvable separation between the rings when the diameter of the largest resolvable ring in the photograph has been determined. The apparatus which has been evolved for this method is described and some results obtained with it are set out.

A Photographic Method for Measuring the Temperature of Light Sources

S. G. Grenishin, A. A. Solodovnikov, and G. P. Startsev, *Trudy Komiss. po Pirometrii pri Vsesoyuz. Nauch.-Issled. Institut. Metrol.*, pp. 57–68, No. 1 (1958) (in Russian)

Some photographic methods of measuring brightness temperature and color temperature are described. For the determination of brightness temperature of the surface of luminous transparent bodies, a method is possible which is based on the comparison of photographic densities formed by unknown and standard light sources, within the limits of a fairly narrow spectral region, subsequently referring the results to the given wavelength. In essence, the practical realization of this method depends on a number of simplified assumptions, in particular, on the linear relation between the density and exposure; Wien's law is used for the spectral distribution of the energy of radiation, but, at temperatures higher than 4000°K, it is necessary to use Planck's law, determining the light flux by means of numerical integration. Consideration is given to the possibilities of also determining the brightness temperature in the case of cavity radiation. For determining the color temperature, the authors propose two methods: by using the "blue/red" ratio (i.e., the ratio of the brightness in two sufficiently separated parts of the spectrum); and by the relative spectral distribution of energy (i.e., the linear relation between log $(B_\lambda \cdot \lambda^5)$ and $1/T$, derived from Wien's law). In the first case, to obtain the required data, it is essential to take into account departures from additivity of the photographic action of radiation with different spectral compositions; and in the second, that Wien's law, the limits of which are restricted, is observed. Photographic errors (nonuniformities of the emulsions and their development) depend on the magnitude of the measured temperature: at 10,000°K they do not exceed ± 1.5% for brightness temperature and ± 6% for color temperature.

Simultaneous Determination of the Coefficient of Conductivity of Heat and the Moisture Content of an Emulsion

A. V. Lykov and F. M. Polonskaya, *Trudy Vsesoyuz. Nauch.-Issled. Kinofotoinst.*, pp. 5–10, No. 6(16) (1957)

A method has been worked out and apparatus has been constructed for the simultaneous determination of the coefficient of conductivity of heat, k, and moisture content of a photographic emulsion without destroying its structure during drying. In the method, a single-valued relationship is assumed between changes in the moisture content and in the thermal characteristics of the material at a constant temperature, and in particular in the expression for k. Heating is carried out by the passage of short (10 to 15 sec) impulses of current through a constantan wire, with which is combined a wire of a copper-constantan thermocouple. There are several such combined pairs of wires in the apparatus, as a consequence of which it is possible to take the moisture content in the whole volume of the material being studied. For calibration, filter paper is used as a standard. For the evaluation of the instrument, results obtained with it were compared with results obtained by the drying method; the discrepancy between them did not exceed 5%.

The Detection of Statistically Defined Patterns in a Matrix of Dots

B. F. Green, Jr., A. K. Wolf, and B. W. White, *Am. J. Psychol.*, **72**:503–520 (1959).

An investigation was made of the detection ability of observers for visible signals in a random array of visible noise at low signal-to-noise ratios. Test objects consisted of square matrices of dot patterns forming signals of either horizontal or vertical bars. Alternate bars of a given pattern were assigned different probabilities so that each display contained dots at any specific position which were independent and the display was essentially a random sample from a set of independent binomial distributions. The parameters varied were (a) signal-to-noise ratio, (b) duration of exposure, (c) average dot probability, (d) visual subtense, (e)

grain of the display, (f) number of bars comprising the signal, and (g) number of exposures. It was concluded that: (1) exposure durations below but not above 1 sec had a differential effect; (2) individual differences were slight; (3) for fixed matrix size and varying dot probabilities, thresholds (75% differential) of detection were proportional to the standard deviation of the binomial distributions governing the occurrence of the dots; (4) for fixed dot probability and varying grain, the thresholds were inversely related to the grain, but different forms of the relationship were obtained for two different ways of altering grain; (5) over a wide range, visual angle had no significant effect on detectability; (6) the curve relating the threshold to the number of bars in the pattern was U-shaped; (7) patterns with random phase and fixed phase were equally detectable; (8) a small but significant improvement in detectability resulted from a motion-picture display of several independent samples of a pattern.—*C. J. Bartleson*

Test and Measurement Procedures in the Production of Photographic Objectives

G. BARNSTEDT, *Hausmitteilungen, Jos. Schneider & Co. Optische Werke*, **11**:61–72, 73–96, 98–120, 142–148 (1959)

Modern lens-testing methods, developed to meet present requirements of high-precision production, are described. To measure refractive index, collimated monochromatic light is passed through a prism constructed of the material being tested. Measurement of the entrance and exit angles leads to the desired index value. Refractometers of the Pulfrich or Abbe type are also employed, these being quick to use but less accurate than the simple prism method. To measure the refractive index of a lens (without deforming its shape), the lens is surrounded with a liquid (by trial and error) such that passage of a light beam through it indicates that the presence of the lens leaves no effect. Then the index of the liquid can be measured, and this must equal that of the lens. Curvature radii are measured by various types of spherometers, the type chosen depending on the degree of accuracy desired. A geometrical-optical method of curvature measurement is also based on reflection at the test surface. A third method involving autocollimation and interference, and another based on Newton's rings are also used. For thickness measurements, a mechanical method and a pneumatic method are available. As for optical constants, such as the image position, several methods are available, involving visual, photographic, and photoelectric techniques. The position of the best image plane depends not only on the position of the object, but also on whether high contrast or high resolution is desired or some compromise between them. There are four methods to choose from in determining focal length. In the measurement of image errors, the tests of Hartmann, Wetthauer, and the polarization method of Rosenhauer should be mentioned. Photomicrographs of star images are also valuable, as are images of periodic test objects with which the contrast-transfer function of the optical system can be determined.—*E. W. Marchand*

1960 Rapid Processing Symposium 14–15 October

Shoreham Hotel, Washington, D.C.

The Society will hold a Rapid Processing Symposium at the Shoreham Hotel, Washington, D.C., on October 14 and 15 of this year, in cooperation with the Fifth International High-Speed Congress, which will be held in Washington October 16–22. A major goal of the Symposium is the exchange of information relative to: compact, simplified photoprocessing equipment with short access time; special techniques associated with the development and design, the photographic chemistry involved, and the manner of utilization; and, possibly, new features in the design and construction of larger processing machines, and advances in processing methods and control techniques. Exhibit space will be available at a nominal fee for the display and operation of related equipment.

The Papers Program is being prepared under the guidance of — *Papers Chairman:* Fordyce M. Brown, Photomechanisms, Inc., Box 67, Huntington Station, L.I., N.Y.

Among others who are responsible for the Symposium are —

Conference Coordinator: Ira R. Kohlman, Colorfax Laboratories, Inc., 1160 Bonifant St., Silver Spring, Md.

Registration Chairman: Joseph Mangiaracina, 30 Brook Ave., Little Silver, N.J.

Program Chairman: Dwin R. Craig, LogEtronics, Inc., 500 E. Monroe Ave., Alexandria, Va.

Publicity Chairman: E. F. Richner, Eastman Kodak Co., 343 State St., Rochester 4, N.Y.

• New Products and Developments

FRANK SMITH

• Cameras and Accessories

16mm Cine-Fluorographic Camera

Photomechanisms Inc., Huntington Station, N.Y., has announced Model 360-1, 16mm cine-fluorographic camera, designed to photograph the output of various x-ray fluorographic image-intensifying tubes. The camera is a modified Cine-Kodak K-100 Camera with a phase-polarized synchronous drive which provides rates of 60, 15, and $7^1/_2$ frames/sec, and two commutator control circuits for synchronizing associated equipment. The camera, with drive, is 6.06 in. wide by 8.37 in. by 9.00 in. high and weighs $14^1/_2$ lb without the lens.

Camera-Processor-Viewer

Optomechanisms Inc., 216 East Second St., Mineola, N.Y., has announced the Camera-Processor-Viewer Model 194A, which is designed to expose and rapidly process film, and then project the image onto a viewing screen. It is a stepwise device in which the cycle of operation is started from an input command pulse, locally or remotely initiated.

Processing temperatures from 68°F to 160°F can be used, with times as short as 2-sec development and 2-sec fixing. A water rinse is applied in a transparent projection cell.

The processing baths are contained in plug-in tank assemblies, each of which contains two immersed gear pumps, heaters, adjustable thermostatic control, quick-disconnect fluid lines, and electrical connectors. The unit is $20^1/_2$ in. high by 15 in. deep by $16^1/_2$ in. wide and weighs approximately 40 lb.

165° Lens for 16mm Cameras

Traid Corporation, Encino, Calif., has announced Model 730A Periphoto 165° Lens, which is an $f/1.5$ nine-element reverse telephoto design with a focal length of 3.45 mm. The distortion at 70° half-angle is 62%. The lens is built for rugged duty, such as rough drone landings, and is attached to the camera with a three-screw, heavy-duty steel, GSAP-type mounting bracket. The lens is watertight and is equipped with antifoggant purging ports and fiducial marker. The reflection-reducing coating is magnesium fluoride, and the lens is color corrected for Daylight Kodachrome.

Portable High-Speed Electronic Framing Camera

The Model 1 High-Speed Framing Camera, which is 12 in. by 18 in. by 22 in. and weighs 40 lb, has been announced by Abtronics, Inc., Livermore, Calif. The camera uses image-converter tube shutters which provide exposure times of 0.1 to 10 μsec. A separate shutter tube and objective lens is used for each exposure, providing, in effect, the equivalent of four independent cameras.

Each of the four channels has separate focus and aperture adjustments, and an independent time delay adjustable from 1 to 1000 μsec. Four exposures can be made in sequence or simultaneously.

The camera is equipped with four $f/1.4$ Nikkor 50mm objective lenses, and a Wollensak 75mm $f/1.9$ recording lens.

Variable Focus Lens

Traid Corporation, Encino, Calif., has announced a variable focus lens, designated the "Twenty-Eighty," for 16mm cameras. The $f/2.5$ lens, which is $4^1/_2$ in. long with a 2-in. diam., has a range of focal lengths from 20mm to 80mm, with constant iris for the same exposure throughout the focal range, a control lever for zooming, and focusing scale with settings from 48 in. to infinity. It fits any 16mm camera with a "C" mount.

Fastax High-Speed 35mm Camera

Wollensak Optical Co., Rochester 21, N.Y., has announced the WF 8A 35mm Fastax high-speed motion-picture camera with 400-ft film capacity. The camera has 8 speeds from 200 to 2000 frames/sec, and produces full-frame pictures. Features of the camera include push-button speed selection, rotating prism, high efficiency coaxial drum shutter, rapid acceleration, three optically projected fiducial markers, and through-the-lens viewfinder.

The camera is equipped with a $5^3/_8$ in. $f/3.5$ Fastax Pro-Raptar Lens in focusing mount, is 22 in. by 25 in. by $12^1/_2$ in. with magazine, and weighs 87 lb with motor.

Waddell High-Speed Cameras

The Ultra High-Speed Recording Streak Camera designed by John H. Waddell, Inc., Syosset, N.Y., consists of two parts: the optical system, including lenses, rotating mirror, gear train, and motor; and the housing, which is built to order. The camera housing diameter will vary, depending on the recording speed required for the streak image. The camera is regularly equipped to operate on 115-v alternating or direct current, although a 28-v motor can be supplied for airborne operation. The motor is coupled through a gear train to a shaft which will rotate up to 3000 rps, and a reflecting prism is mounted to the end of the shaft. The objective lens is focused on a slit; the image formed at the slit is relayed by a lens and the reflecting prism to the inner surface of the camera housing. The film is in a track on the inside circumference of the housing.

The Controlled Speed 16mm High-Speed Camera can be operated at 1000, 2000, 3000 or 4000 frames/sec within ±5%, and can be stopped and started at any of these rates.

Although the information contained in this section is compiled from sources believed to be reliable, the author cannot assume responsibility for its accuracy. Publication of the information here is not to be construed as an endorsement or recommendation of the product or equipment described.

• Processing

Rapromatic Processing System

Specialties, Inc., Skunks Misery Road, Syosset, N.Y., has developed a method for processing motion-picture roll film in a magazine-processor attached to the camera, using a porous web material saturated with a monobath. In operation, the processing solution is applied to the emulsion by sandwiching the photographic material with the paper web, called Raproroll. The paper releases its liquid under pressure and the liquid is accepted by the emulsion. Since the required quantity of solution is controlled by web thickness and composition, there is no dripping.

A compact, simple to operate, Table Processor, has also been developed which will accept 400 ft of either 16mm or 35mm film.

• Reproduction and Copying

Electronic Flash Color Reproduction System

The Repronar, a color-transparency copying device, has been developed by the Heiland Division of Minneapolis-Honeywell Regulator Company. The unit resembles an enlarger, with an electronic flash unit concealed in the easel or base.

The Repronar consists of a 35mm single-lens reflex camera with $f/3.5$ lens, an easel with slide and filter holders, an incandescent light source for transparency viewing, and an electronic Strobonar unit for actual exposing. A calibrated scale indicates proper exposure from the magnification selected. Only the lens opening is adjusted for exposure, since the electronic-flash light source has a constant time of $^1/_{2000}$th sec, and the camera shutter a fixed speed of $^1/_{50}$th sec.

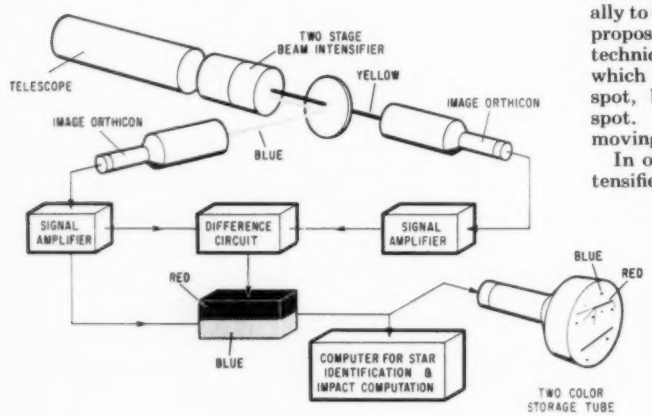
Remington Rand Film-a-Record Micro-Station Package Plan

A microfilm package plan that includes camera, film, processor, protective jackets, and reader has been announced by the Remington Rand Division of Sperry Rand Corp., 315 Park Avenue South, New York 10.

The F 36.1 PL camera microfilms engineering drawings from 15 by 21 in. to 36 by 47 in., at reductions of 12 to 29 times. An exposure meter is provided.

The Unipro Microfilm Processor develops, fixes, washes, and dries 16mm, 35mm, and 70mm film of any length up to 100 ft. The processor is loaded and operated in normal light, and will process 100 ft of film in less than half an hour.

An acetate jacket called the Uni-Kard, is provided for filing and protecting individual images.



• Miscellaneous

Reconofax System for Aerial Photos at Night

The Reconofax system, developed by HRB-Singer, Inc., State College, Pa., makes use of a scanning camera with an infrared detector which modulates a recording lamp. Since all objects on the ground, including military targets, emit infrared radiation, the device provides a means of producing night photographs for reconnaissance purposes. An advantage of infrared is its ability to detect radiation which is not visible, thus providing a possible means of camouflage detection.

Reconofax can also be used to photograph moving targets while the scanner is held stationary. Applications of this include traffic control, assembly line inspection, and burglar alarms.

X-Ray Time-Lapse Studies of Living Bone

A method which shows x-ray changes of living bone as a motion picture has been developed by Dr. Howard J. Barnhard, radiologist at Hahnemann Hospital, Philadelphia.

To demonstrate the method, x-rays were made of a dog's foreleg every four hours, with the leg, x-ray equipment and film held in exactly the same positions. Subsequently, these x-rays were photographed in sequence on motion picture film. When projected, the bone changes are seen at increased rate.

"A Celestial Moving Target Indicator"

H. Dubner, J. Bramley and N. Sclar of Avion Division, ACF Industries, Inc., Paramus, N.J., in a paper of the above title, presented at the Sixth National Annual Meeting of the American Astronautical Society, Jan. 18–21, 1960, in New York City, proposed a celestial moving target indicator which detects a moving luminous source against a star background by discriminating against the stationary star sources. (See illustration at left.)

The present astronomical technique for detection of moving luminous objects is to photograph the same portion of the sky over several time intervals and then visually to compare the pictures. In place of this, the authors propose a Celestial Moving Target Indicator (CMTI) technique based on a characteristic of the P-7 phosphor which fluoresces blue-white for a continuously activated spot, but phosphoresces yellow at a recently vacated spot. Fixed stars, therefore, appear blue-white while moving targets leave a yellow trail.

In operation, the sky field is imaged onto a beam intensifier whose output is a P-7 phosphor screen. The resultant light output is viewed with a two-color TV orthicon which gives a signal for the blue separate from that of the yellow.

Although the technique is particularly applicable to orbiting satellites, it can also be used for tracking rockets during their boost phase and for missiles carrying flash bombs. The range capability is of the order of thousands of miles.

Radar Mapping System

In the AN/APQ-55 side-looking radar system, developed for the Air Force by Texas Instruments, Inc., Dallas, radar returns are displayed as a single modulated trace on a cathode-ray tube and recorded on film which is moving continuously at a rate proportional to the ground speed and altitude of the aircraft.

The perspective is adjusted electronically so that the scale is the same at the center and edges of the record. A constant ground area is scanned irrespective of altitude. A microwave data link can transmit the radar data from the aircraft to a film recorder and processor on the ground. The system is designed to map from either piloted or unmanned aircraft, at ground speeds of 200 to 800 knots, simultaneously recording strips of terrain, either 3 or 6 miles wide, on both sides of the aircraft.

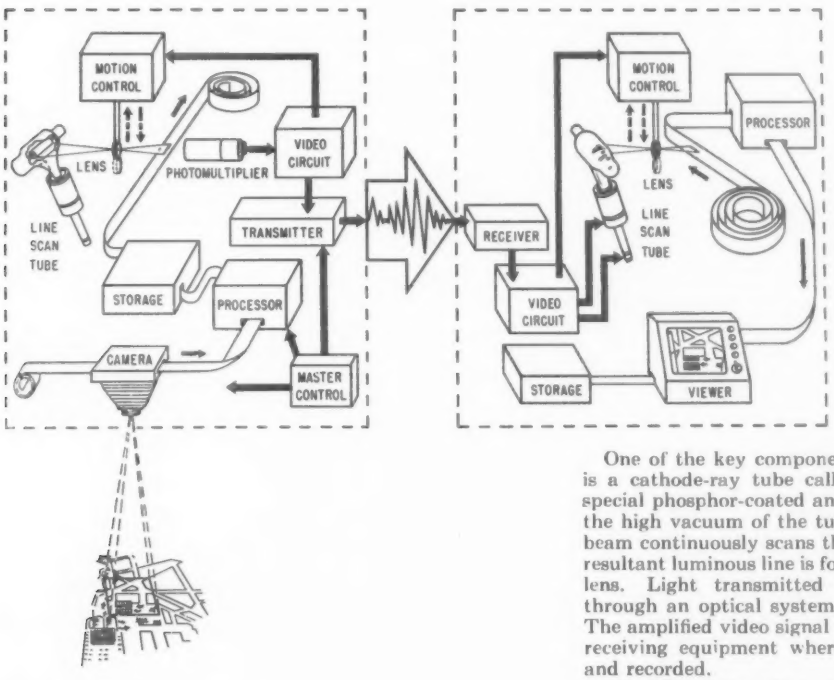
Applications for Electrically Exploded Wire

A variety of applications for electrically exploded wires has been proposed by Electro-Optical Systems, Inc., Pasadena, Calif., as a result of a year-long basic research study in exploding-wire use sponsored by the Army Ordnance Corps.

Exploding wires appear feasible for such applications as high-intensity light sources for communications, propulsive devices for vehicles in outer space environment, and hypervelocity particle impact research. Key to these heat and light applications lies in the technique of switching large currents into thin wires in millimicrosecond time. The technique allows many times the material's vaporization energy to be dumped into the wire, creating temperatures above 100,000°C and pressures in the megabar range. Specific impulses of 1000 sec have been achieved in an exploding aluminum wire, and a 1000 to 5000-sec range appears possible.

Explosion of tungsten wire has provided interesting possibilities for use in space communications, as well as terrestrial searchlight operations. Surface temperatures of 5000°C, coupled with a superheated interior, would give a light source of excellent visibility and large light output.

The Electro-Optical Systems Kerr Cell camera, with an exposure time of 5 mμsec, provides a photographic record of the exploding wire products during the entire explosion period.



CBS Photoscan System for High-Acuity Photo Reconnaissance

In a new high-acuity photo-reconnaissance system called Photoscan, developed at the CBS Laboratories, Stamford, Conn., an airborne electronic scanner converts the visual image obtained from an aerial camera or other sensing device to an electronic signal; the signal is then transmitted to another airborne relay station or directly to receiving equipment on the ground for nearly instantaneous viewing and storage on film.

One of the key components of the Photoscan System is a cathode-ray tube called the Line Scan Tube. A special phosphor-coated anode spins at 1600 rpm within the high vacuum of the tube envelope. A fine electron beam continuously scans the rotating phosphor, and the resultant luminous line is focused on the film by a moving lens. Light transmitted by the film is transferred through an optical system into a photomultiplier tube. The amplified video signal is then transmitted to distant receiving equipment where the image is reconstituted and recorded.

The Photoscan pictures have definition in excess of 10,000 lines, as compared to 500 line resolution of conventional television techniques.

Although photographic film provides the best medium for the high-resolution image, any recording material which will effectively modulate light—e.g., xerographic plates—may be used in place of film. Under certain conditions, light-reflective paper may be used.

The Fairchild Camera & Instrument Corp., Syosset, L.I., N.Y., will supply the aerial cameras and rapid film processor, and is responsible for the installation of the over-all system.

• SPSE Journal Award

William West and Vernon Saunders of the Kodak Research Laboratories have received the 1960 SPSE Journal Award "for the best technical paper published in *Photographic Science and Engineering*" during 1959. Their paper, "Experimental Studies of the Mode of Action of Sensitizing Impurities in Thin Crystals of Silver Bromide," appeared in the November-December issue (*P S & E*, **3:** 258). It dealt with the behavior of trace materials in silver bromide and their role in photographic sensitivity.

William West

Vernon I. Saunders

Dr. West, a senior research associate in the photographic theory division of Kodak Research Laboratories, Rochester, N.Y., was born in Scotland and educated at the University of Edinburgh. He later did research at Columbia University and served on the faculty of Washington Square College of New York University. He joined Eastman Kodak Co. in 1941, first working with the emulsion research laboratory, and then taking up work in photographic theory. In 1942–43, he was on leave of absence to do war research at Columbia University.

Dr. West is a Fellow of the New York Academy of Sciences and a member of other scientific groups, including the Faraday Society, Phi Lambda Upsilon, honorary chemical fraternity, and Sigma Xi, honorary scientific fraternity. He has published some 35 papers dealing with spectroscopy, photochemistry, and general physical chemistry, and has spoken at numerous scientific meetings in the United States and Europe.

Vernon Saunders, a research associate in the Kodak Research Laboratories, was graduated from the University of Western Ontario, London, Ontario, where he received a Master of Science degree in chemistry in 1946.

He began at Kodak in 1948, working on filter dyes in the emulsion research division of the laboratories in Rochester. In 1955, he joined the photographic theory division, where he has been associated with Dr. West on research into the mechanism of latent image formation and photographic theory.

The award to Dr. West and Mr. Saunders was announced at the Annual Conference at Santa Monica on May 12th. At the same time, two other papers were accorded Honorable Mention: "Photothermographic Sensitization of Mercurous Oxalate by Mercurous and Silver Iodides," by Paul B. Gilman, Jr., Philip A. Vaughan, and P. A. van der Meulen of Rutgers, the State University, New Jersey (*P S & E*, **3:** 215); and "Layer Thickness of Photographic Emulsions and Image Definition," by H. F. Nitka and A. J. Derr of the Ansco Research Laboratories (*P S & E*, **3:** 1).

• Notes from the Editor

SPSE Honors

At the 1960 Annual Conference in Santa Monica, May 12, Dr. Douglas A. Spencer was made an Honorary Member of the Society (see p. 185), and Fellowships were conferred on Dr. R. Clark Jones, "research physicist, prolific author, and expert on radiation detectors," Dr. Herman H. Duerr, "specialist in sensitized products and outstanding leader in the field of photographic chemical research," Ralph M. Evans, "scientist, author, and outstanding lecturer on visual effects in color photography," and Dean C. B. Neblette, "author and teacher par excellence." Peter Krause and Carl R. Markwith were awarded Senior Memberships.

Photographic Aids in Archaeology

Photographic methods which can greatly facilitate the investigations of ancient tombs are described (without technical details) in a beautifully illustrated article by Carlo M. Lerici, "Periscope on the Etruscan Past," published in *The National Geographic Magazine*, CXVI: 336–50, Sept. 1959. A study of aerial photographs taken by British fliers in Italy during World War II had revealed extensive Etruscan burial grounds which had completely escaped detection from the ground. A further use of photographic methods enables the archaeologist to obtain photographs of the interior of the tombs before any excavation is attempted; thus useless excavation of empty or hopelessly disintegrated tombs can be avoided. The "photographic drill," which is lowered into the tomb through a hole made by an electric drill, consists of a three-inch aluminum tube fitted with a tiny Minox camera and a high-intensity photoflash unit. The flash and camera are triggered by remote control. The entire interior of the tomb can be photographed in 12 shots, the tube being turned 30° after each shot.

The Society of Photographic Scientists and Engineers

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